

PATENT APPLICATION  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 2950.20US01

Chaloner-Gill et al.

Confirmation No.: 2942

Application No.: 09/845,985

Examiner: Mark Ruthkosky

Filed: April 30, 2001

Group Art Unit: 1745

For: PHOSPHATE POWDER COMPOSITIONS AND METHODS FOR FORMING PARTICLES  
WITH COMPLEX ANIONS

---

DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendments  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

We, Craig R. Horne, Ph.D. and On K. Chang, Ph.D., hereby declare as follows:

1. Craig R. Horne, Ph.D. is presently Director, Electrochemical Applications at NanoGram, Corp. Dr. Horne was awarded his Ph.D. in Materials Science & Mineral Engineering from the University of California, Berkeley in 2000. Dr. Horne has eight published technical papers, has been active in the Electrochemical Society and has referred papers for the Journal of the Electrochemical Society. Dr. Horne has been an employee or consultant to NanoGram, its parent company NeoPhotonics or its majority owned subsidiary Kainos Energy Corporation since he departed Berkeley in 1998. Dr. Horne is an inventor on 10 issued U.S. Patents and numerous U.S. and foreign pending applications. More details on Dr. Horne's qualifications are found on the attached resume.
2. On K. Chang, Ph.D., is presently a consultant for NanoGram Corp. Dr. Chang received his Ph.D. from the University of California, Davis in Physical Chemistry in 1985. Dr. Chang has nine scientific publications and has worked extensively in the battery and battery materials area

BEST AVAILABLE COPY

Application No. 09/845,985

from 1986 to the present. In particular, except for two years working on semiconductor packaging, Dr. Chang has worked in the battery areas for this entire time. Dr. Chang is an inventor on 20 issued U.S. Patents. More details on Dr. Chang's qualifications are found on the attached resume.

3. Dr. Horne is an inventor on the patent application noted above that is presently under examination. Dr. Chang is not an inventor on this patent application. However, he has reviewed the pending claims in this application.

4. We have carefully read U.S. Patent 5,538,814 to Kamauchi et al. (the Kamauchi patent). We have reproduced the formation of lithium cobalt phosphate based on the teachings of the Kamauchi patent. Specifically, we followed a procedure similar to the procedure of Example 1 of the Kamauchi patent. Thus, we mixed lithium carbonate, cobalt carbonate hydrate and 85% phosphoric acid to achieve an atomic ratio of  $\text{Li}:\text{Co}:\text{P} = 2:1:1$ . We used cobalt carbonate hydrate as a substitute for basic cobalt carbonate, which generally has cobalt hydroxide as a contaminant, due to its higher purity. As noted in the Example, this results in a mixed phase material comprising lithium phosphate, lithium-cobalt phosphate and cobalt oxide. As described in the Kamauchi patent, the reaction mixture was heated at  $900^{\circ}\text{C}$  for 24 hours. Further details are in the attached report.

5. In addition to the formation of lithium cobalt phosphate, we also synthesized lithium iron phosphate using techniques similar to known approaches and the approach in the Kamauchi patent. Specifically, the  $\text{LiFePO}_4$  was synthesized using the procedure in the Kamauchi patent with some revisions based on a procedure published in an article by A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as Positive Electrode Materials for Rechargeable Lithium Batteries," *J. Electrochemical Society*, 144(4): 1188-1193 (1997). Our synthesis reaction involved Fe(II) oxide, 85% phosphoric acid and lithium carbonate. Iron (II) carbonate, corresponding to the cobalt carbonate of the Kamauchi process, is not commercially available and is thought to be unstable due to spontaneous decomposition to iron oxide and carbon dioxide. Also, iron (II) oxide is known to react with phosphoric acid to form iron phosphate so it seemed to be an appropriate reactant. Phosphoric acid was used since it was used

Application No. 09/845,985

in the Kamauchi patent. Relative to the Padhi et al. process, we substituted Fe(II) oxide for Fe(II) acetate and 85% phosphoric acid for ammonium phosphate. In our synthesis reaction, an initial heating step was performed at 300 to 350°C, which was followed by heating at 800°C for 24 hours. The heating was done in a nitrogen environment, as taught in Padhi et al. since it is thought that heating in the presence of oxygen would form Fe(III). The resulting composition was confirmed with an x-ray diffractogram so that the substitutions did not change the product composition. Further details are in the attached report.

6. The as synthesized phosphate powders were processed using ball milling. The Kamauchi patent does not describe their milling techniques in detail. However, Example 7 at column 18 describes ball milling as a suitable milling approach. Similarly, Example 10 describes milling in a ball mill for 24 hours. This is the approach that we adopted for processing of the phosphate powders. A commercial ball mill was used, and the powders were milled for 24 hours. The results of our phosphate particle processing is described in detail in the attached report entitled "Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO<sub>4</sub>) and Lithium Iron Phosphate (LiFePO<sub>4</sub>)." The results of which are summarized in the following.


7. The ground phosphate powders were evaluated using both visual evaluation of scanning electron micrographs (SEM) and light scattering of powders dispersed in a liquid. Transmission electron micrographs were not obtained since these would not have been meaningful beyond the SEM photos due to the large particles in the samples and the large range of particle sizes. The non-uniformity of the powders is readily observable in the SEM photographs, which clearly show tiny particles as well as relatively large chunks. These results are consistent with the light scattering results, which clearly show a very broad distribution of particle sizes. Plots in the attached report show the particle size distribution by volume as well as by particle number for the two phosphate samples. The light scattering results were performed with an ultrasonic probe to break agglomerates. This state of the art dispersion approach should be very effective at separating particles within agglomerates. The light scattering measurements were performed by an independent contractor based on samples that we provided.

Application No. 09/845,985

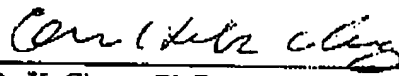
8. These particle size measurements clearly demonstrate that conventional grinding approaches cannot produce phosphate powders with close to the uniformity of the phosphate powders claimed in the pending claims of the present application.

9. We each independently declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Apr 5 2006  
Date

  
Craig R. Home, Ph.D.

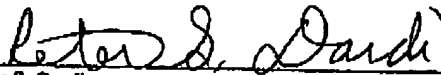
Apr. 5 2006  
Date

  
On K. Chang, Ph.D.

## CERTIFICATE OF FACSIMILE TRANSMISSION

I hereby certify that this paper is being transmitted by facsimile to the U.S. Patent and Trademark Office. Fax No. 571-273-8300 on the date shown below thereby constituting filing of same.

April 6, 2006  
Date

  
Peter S. Dardi

## **Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO<sub>4</sub>) and Lithium Iron Phosphate (LiFePO<sub>4</sub>)**

On Chang and Craig Horne

NanoGram Corporation

### **BACKGROUND**

The purpose of this experiment is to evaluate the particle size distribution of metal phosphate nanoscale particles produced by following the teaching of U.S. Patent 5,538,814, the Kamauchi patent. For completeness, this demonstration was performed on two separate metal phosphate systems: (a) the Li-Co-PO<sub>4</sub> mixed-phase material that is the specific example in the Kamauchi patent, and (b) LiFePO<sub>4</sub>.

### **EXPERIMENTAL**

#### **Chemicals**

Cobalt (II) carbonate hydrated: Sigma-Aldrich, Cat. No. 202193, Lot No. 05130JC  
Lithium carbonate: Sigma-Aldrich, Cat. No. 255823, 99% ACS grade, Lot No. 08004KC  
Phosphoric acid: Ashland chemical, 85%, semiconductor grade  
Iron (II) Oxide: Sigma-Aldrich, Cat. No. 400866, 99.9%, Lot No. 13722PC

#### **Equipment**

Jar mill: One-tier jar high-capacity laboratory jar mill, 13" roller, Cole Parmer, Cat. No. EW-04149-00  
Milling jar: HDPE milling jar, 0.25 gal, with ridges on the interior to improve tumbling of the grinding media. Cole Parmer Cat. No. EW-04172-02  
Milling jar sleeve: Milling jar sleeve, Cole Parmer Cat. No. EW-04172-12  
Grinding media: Zirconia grinding media, 3/8" x 3/8. Cole Parmer Cat. No. EW-04158-10. About 2.37kg (750 pieces) of the grinding media were used per milling jar.  
Sieve: USA standard test sieve, No 10. (2mm). Stainless steel frame and wire, 8" diameter. Cole Parmer Cat. No. EW-59984-01.

#### **Approach**

The chemical precursors were first evaluated to determine the molar amount of metal per unit weight of precursor. The established molar quantities were then used to determine the precursor quantities yielding the desired metal ratio. The respective precursors were weighed and mixed, calcined, and finally milled following the methods prescribed in the Kamauchi patent. The synthesized materials were analyzed for phase content by X-ray diffraction and particle size by several methods.

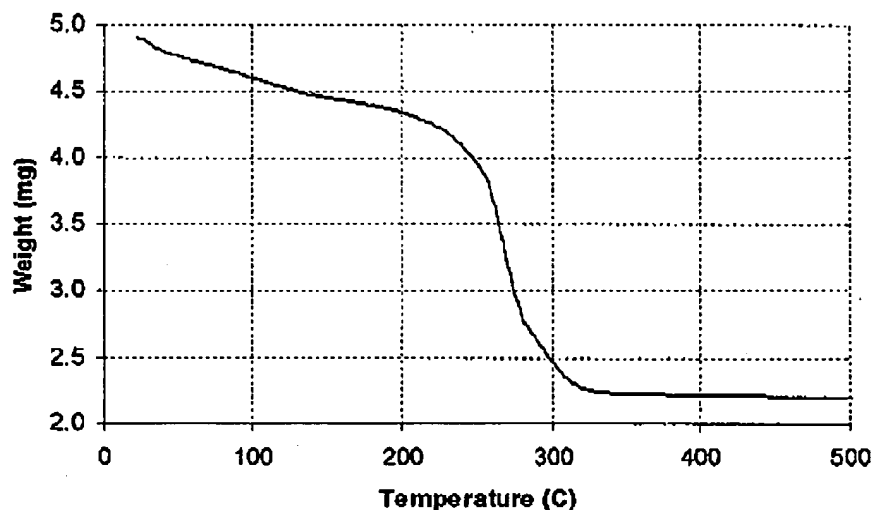
### **RESULTS AND DISCUSSION**

#### **Precursor Analysis**

The cobalt (II) carbonate hydrated as purchased contains unknown amount of hydrated water. It is necessary to determine the water content in order to achieve an accurate stoichiometry.

Before the analysis, it is necessary to allow the cobalt (II) carbonate sample to reach equilibrium with normal lab atmosphere so that no water will be gained or lost during sample handling. To achieve this, about 20 g of cobalt (II) carbonate was placed on a dish and exposed to normal lab atmosphere for 14 hours. Then the exposed cobalt (II) carbonate was analyzed with TGA (thermogravimetric analyzer) to determine the water content from the weight loss. The TGA ramp rate was 10C/min. The atmosphere was 4% H<sub>2</sub> in N<sub>2</sub>. The result is shown in Figure 1.

Figure 1. TGA Curve of Cobalt (II) Carbonate Hydrated



The total wt loss from room temp to 500C was about 54.8%, corresponding to CoCO<sub>3</sub> 8.0 H<sub>2</sub>O (MW= 262.9). The amount of water in excess of the amount corresponding to the known hexa-hydrated form (see, for example "Merck Index") is probably due to absorbed water. Since water of hydration does not form with Li<sub>2</sub>CO<sub>3</sub> or FeO, and the P precursor was in liquid form, this analysis was not required to generate the necessary molar quantities of lithium, iron, or phosphorous per gram of their respective precursors.

#### Synthesis of materials

The respective precursor chemicals were used for the synthesis of Li-Co-PO<sub>4</sub> and LiFePO<sub>4</sub> according to the teachings of the Kamauchi patent. Note that the precursor mixing method used in this experiment, grinding in a mortar and pestle, is more detailed and thorough than that described in the Kamauchi patent (see Appendix A). The mortar and pestle mixing employed in this experiment tends to reduce precursor particle size. Therefore, this approach will help minimize product particle size thus making the experiment more favorable towards achieving the results asserted in the Kamauchi patent.

#### Synthesis of Li-Co-PO<sub>4</sub> mixed-phase material

According to the Kamauchi patent, it is understood that the product, hereafter referred to as Li-Co-PO<sub>4</sub> positive electrode material mix, is not a pure phase, but is a mixture of lithium phosphate, lithium cobalt phosphate, and lithium cobalt oxide. The amounts of

starting materials actually used in this experiment are shown in Table 1 and yielded a Li:Co:P atomic (mole) ratio of 2:1:1. The atomic ratio used matches that used in Example 1 of the Kamauchi patent (Appendix A).

Table 1. Amounts of Starting Materials for the Synthesis of Li-Co-PO<sub>4</sub> Material Mix

Materials	Molar mass	Wt (g) used	Moles	Atomic ratio
Li <sub>2</sub> CO <sub>3</sub>	73.88	4.984	0.06746	2.00
CoCO <sub>3</sub> 8.0 H <sub>2</sub> O	262.9	17.75	0.06752	1.00
H <sub>3</sub> PO <sub>4</sub> , 85% solution	98.00	7.785	0.06752	1.00

Li<sub>2</sub>CO<sub>3</sub> and CoCO<sub>3</sub> 8.0 H<sub>2</sub>O were weighed out and mixed with mortar and pestle for about 10 minutes. After grinding, the color was uniformly pink. Then phosphoric acid was added and mixing continued for another 20 minutes. Within a few minutes after adding phosphoric acid, foaming due to generation of CO<sub>2</sub> was observed. After the mixing, the powder appeared dry. The color was pink.

The mix was then placed in a crucible and heated in the furnace. The temperature was ramped up at 10 C/min to 900 C, then held at 900 C for 24 hours. The weight of the reaction mix before heating was 29.535g. The weight of the product mix after heating was 17.382g. After heating, the product was in the form of a soft cake of powder. The color of the product was dark gray. The product was later ground and milled, as described below.

#### Synthesis of LiFePO<sub>4</sub> material

According to a journal article (Padhi, 1997, see Appendix B), the mole ratio of Li, Fe and P should be 1:1:1. The amounts of starting materials actually used in this experiment for the synthesis of LiFePO<sub>4</sub> are shown in Table 2.

Table 2. Amount of Starting Materials for the Synthesis of LiFePO<sub>4</sub>

Materials	Molar mass	Wt (g) used	Moles	Atomic ratio
Li <sub>2</sub> CO <sub>3</sub>	73.88	4.889	0.06617	1.00
FeO	71.85	9.511	0.13237	1.00
H <sub>3</sub> PO <sub>4</sub> , 85% solution	98	15.31	0.1328	1.00

Li<sub>2</sub>CO<sub>3</sub> and FeO were first weighed out and ground together with mortar and pestle for 20 minutes. After grinding, the color was uniformly gray. Then H<sub>3</sub>PO<sub>4</sub> was added. Gas (presumably CO<sub>2</sub>) was generated. After mixing of the above material, the material was dark gray and mud-like. The material was heated under nitrogen at 300°C for one hour. After heating, the material forms brittle lumps. The color was not uniform, from light gray to dark gray. The material was then ground with a mortar and pestle. Then the material was further heated under nitrogen at 800°C for 24 hours. After heating, the product was in the form of a sintered hard cake. The product color was not uniform,

from gray to beige. Some of the material adhered to the crucible tightly and could not be collected. The product was also later ground and milled, as described below.

#### Grinding of materials

The Li-Co-PO<sub>4</sub> positive electrode material mix and the LiFePO<sub>4</sub> were ground using the same method but in two separated jars. The method used followed the teachings of Examples 10, 11, and 12 from the Kamauchi patent. The grinding jar was charged with 2.37kg (750 pieces) of grinding media. The material to be ground was added to the jar. In the case of LiCoPO<sub>4</sub>, the soft cake of material from the heating was crushed by hand and added to the milling jar. In the case of LiFePO<sub>4</sub>, the hard cake of material from the heating was crushed with mortar and pestle until the particle size was less than about 1mm, then added to the milling jar. The jar mill was turned on and adjusted to 150+/-7 rpm. After 24 hours of grinding, the powder was separated from the grinding media with a coarse (2mm) sieve. After grinding, the color of the Li-Co-PO<sub>4</sub> positive electrode material mix powder was dark gray. The color of the LiFePO<sub>4</sub> powder was grayish beige.

#### Phase Analysis via X-ray diffraction

X-ray diffraction measurements were performed on the synthesized and ground materials. The X-ray diffraction patterns are shown in Figures 2 and 3. The pattern of the Li-Co-PO<sub>4</sub> material mix did not match that of LiCoPO<sub>4</sub> from literature. This was expected since it was a mixture. The pattern of the LiFePO<sub>4</sub> material matched XRD patterns for LiFePO<sub>4</sub> in the literature (stick pattern shown by black lines in Figure 3), but some impurity phases could be seen.

Figure 2. X-ray Diffraction Pattern of Li-Co-PO<sub>4</sub> Mixed Phase Material

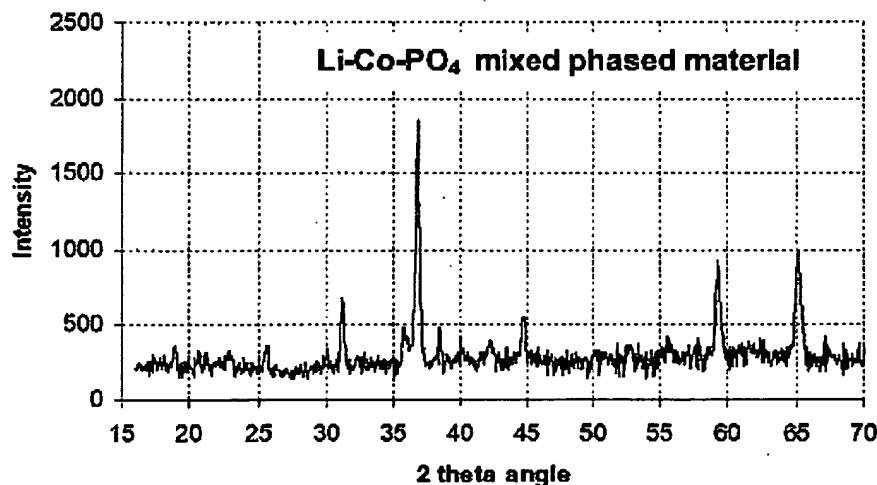
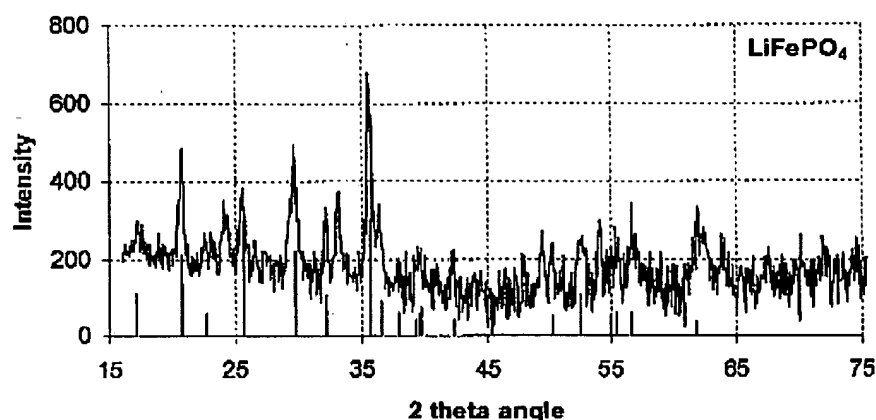




Figure 3. X-ray Diffraction Pattern of  $\text{LiFePO}_4$  Material

#### Particle size analysis

Attempts were made to measure the particle size distribution with the Malvern Zetasizer ZEN3600 particle size analyzer. Approximately 0.1 g of the Li-Co- $\text{PO}_4$  mixed phase sample after 24 hour grinding was added to 20 mL of water. The mix was shaken by hand for 1 minute and sonicated in an ultrasonic bath for 30 minutes. However, during the duration (about 2 minutes) of analysis, a significant portion of the sample precipitated. The Malvern Zetasizer ZEN3600 particle size analyzer is designed for particles small enough not to precipitate out during measurement even without stirring. The fact that Li-Co- $\text{PO}_4$  mixed phase powder precipitated indicated that the particles were too large for the instrument. Because of this difficulty, samples of both the Li-Co- $\text{PO}_4$  mixed phase powder and  $\text{LiFePO}_4$  powder were sent to Micromeritics Analytical Services<sup>1</sup> for particle size analysis by a light scattering technique performed with a Micromeritics Saturn DigiSizer 5200 Particle size analyzer (which has a larger maximum size range than the ZEN3600). General descriptions of the analysis techniques available at Micromeritics are given in Appendix C. Standard method 520-01 (non-aqueous liquid dispersion) was chosen as the method. Isopropanol was chosen as the liquid for two reasons: (1) Isopropanol wets the samples very well. (2) All components, including possible impurities, in the samples are expected to be insoluble in isopropanol.

In the preparation of the dispersion, 2.2g of the sample was added to 80 mL of isopropanol. The dispersion was sonicated using a high intensity (100 W) ultrasonic probe for one minute in order to break any agglomerates of particles. An ultrasonic probe (instead of an ultrasonic bath) was used because of its much higher intensity. The analysis was done twice for each sample. The results reported here are the average of the two analyses. The particle size distribution can be shown as a volume distribution, or as a number distribution. The difference and relationship between the two is explained in Appendix D. The NanoGram patent application describes particle size distributions with

<sup>1</sup> Micromeritics Analytical Services, [www.particletesting.com](http://www.particletesting.com), One Micromeritics Drive, Norcross, Georgia 30093-1877. (770)772-3630

respect to a number distribution. However, it is also common to describe a particle size distribution with respect to volume distribution. Therefore, the data in this experiment is provided both ways. For the two samples, the particle size volume distributions are shown graphically in Figures 4 and 5. The particle size number distributions are shown graphically in Figures 6 and 7. The numerical values of cumulative volume fraction are shown in Tables 3 and 4.

Figure 4. Particle Size Volume Distribution of Li-Co-PO<sub>4</sub> Mixed-Phase Material

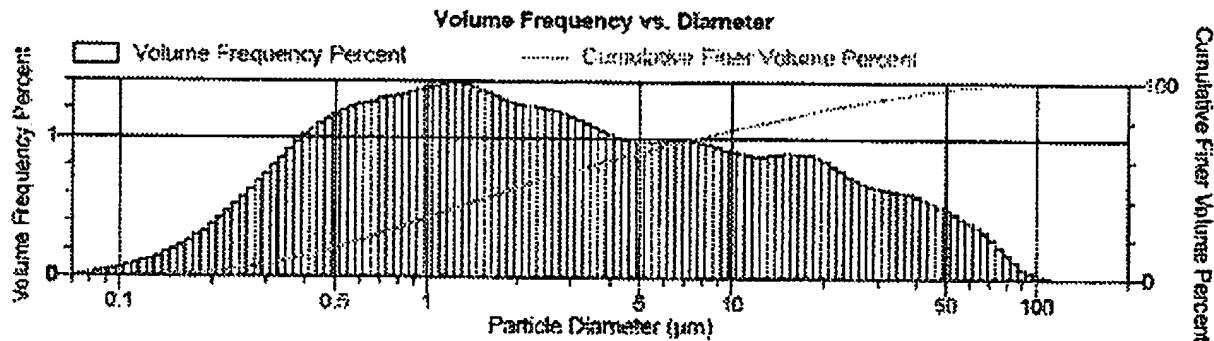


Figure 5. Particle Size Volume Distribution of LiFePO<sub>4</sub> Material

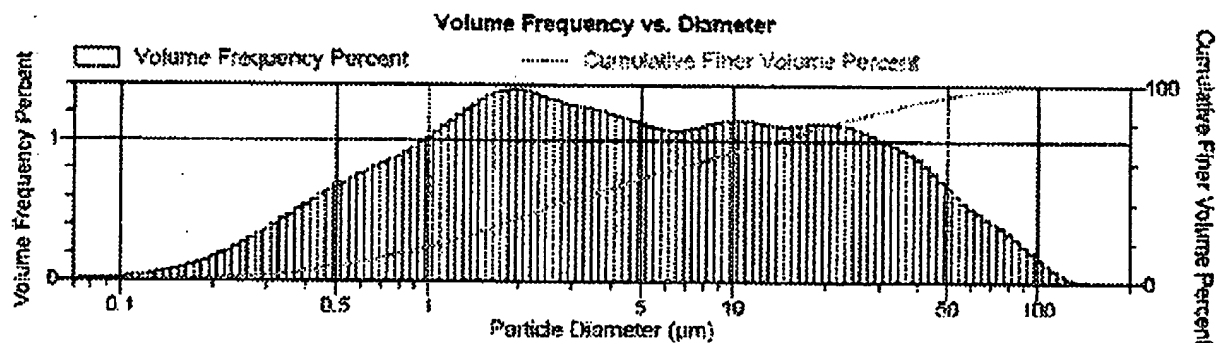


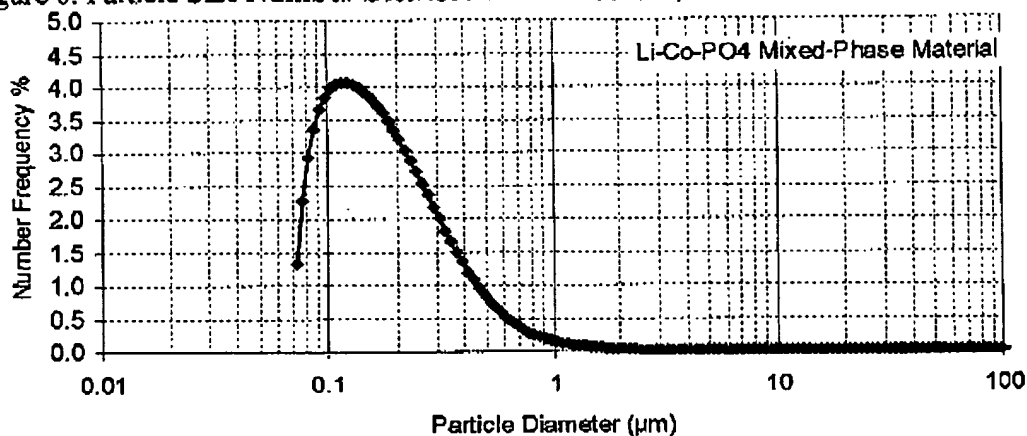
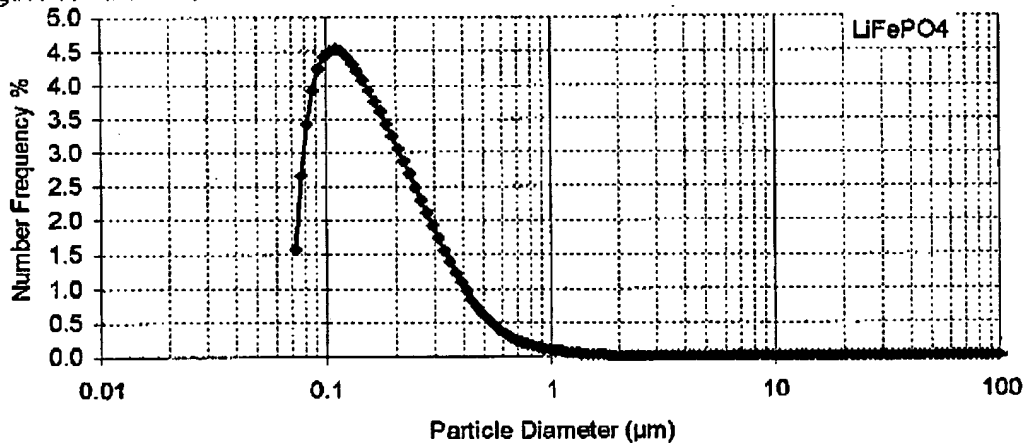
Figure 6. Particle Size Number Distribution of Li-Co-PO<sub>4</sub> Mixed-Phase MaterialFigure 7. Particle Size Number Distribution of LiFePO<sub>4</sub> Material

Table 3. Cumulative Volume Fractions of Li-Co-PO<sub>4</sub> Mixed-Phase Material  
Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size				Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size			
	Test 1	Test 2	Average	Standard Deviation		Test 1	Test 2	Average	Standard Deviation
0.073	0.00%	0.00%	0.00%	0.00%	3.668	45.95%	46.08%	46.02%	0.09%
0.082	0.01%	0.01%	0.01%	0.00%	4.116	48.38%	48.48%	48.43%	0.07%
0.092	0.02%	0.04%	0.03%	0.01%	4.618	50.72%	50.82%	50.77%	0.07%
0.103	0.05%	0.08%	0.07%	0.02%	5.182	52.98%	53.08%	53.03%	0.07%
0.116	0.10%	0.15%	0.12%	0.04%	5.814	55.17%	55.27%	55.22%	0.07%
0.130	0.17%	0.25%	0.21%	0.05%	6.523	57.32%	57.42%	57.37%	0.07%
0.146	0.28%	0.38%	0.33%	0.07%	7.319	59.49%	59.58%	59.53%	0.06%
0.164	0.43%	0.56%	0.50%	0.09%	8.213	61.72%	61.77%	61.75%	0.04%
0.184	0.65%	0.80%	0.73%	0.11%	9.215	64.01%	64.02%	64.02%	0.01%
0.206	0.95%	1.12%	1.04%	0.12%	10.339	66.31%	66.31%	66.31%	0.00%
0.231	1.35%	1.54%	1.44%	0.13%	11.600	68.59%	68.59%	68.59%	0.00%
0.260	1.86%	2.06%	1.96%	0.14%	13.016	70.82%	70.84%	70.83%	0.02%
0.291	2.51%	2.70%	2.61%	0.14%	14.604	73.03%	73.06%	73.04%	0.02%
0.327	3.30%	3.48%	3.39%	0.13%	16.386	75.25%	75.27%	75.26%	0.01%
0.367	4.23%	4.40%	4.32%	0.12%	18.368	77.50%	77.50%	77.50%	0.00%
0.412	5.31%	5.46%	5.38%	0.11%	20.629	79.76%	79.74%	79.75%	0.01%
0.462	6.52%	6.65%	6.59%	0.10%	23.146	82.00%	81.98%	81.99%	0.02%
0.518	7.85%	7.98%	7.91%	0.09%	25.970	84.18%	84.16%	84.17%	0.01%
0.581	9.28%	9.41%	9.35%	0.09%	29.139	86.27%	86.26%	86.27%	0.01%
0.652	10.81%	10.95%	10.88%	0.10%	32.695	88.27%	88.26%	88.27%	0.01%
0.732	12.43%	12.60%	12.52%	0.12%	36.684	90.19%	90.17%	90.18%	0.01%
0.821	14.16%	14.35%	14.26%	0.13%	41.160	91.98%	91.95%	91.96%	0.02%
0.921	16.01%	16.22%	16.12%	0.15%	46.182	93.58%	93.55%	93.56%	0.03%
1.034	18.01%	18.23%	18.12%	0.15%	51.817	94.96%	94.94%	94.95%	0.02%
1.160	20.17%	20.38%	20.27%	0.15%	58.140	96.12%	96.13%	96.12%	0.01%
1.302	22.48%	22.70%	22.59%	0.15%	65.234	97.08%	97.15%	97.11%	0.05%
1.460	24.86%	25.18%	25.06%	0.17%	73.194	97.89%	98.03%	97.96%	0.10%
1.639	27.53%	27.80%	27.66%	0.19%	82.125	98.57%	98.76%	98.67%	0.13%
1.839	30.19%	30.51%	30.35%	0.22%	92.146	99.13%	99.33%	99.23%	0.14%
2.063	32.89%	33.25%	33.07%	0.25%	103.389	99.54%	99.71%	99.63%	0.12%
2.315	35.59%	35.95%	35.77%	0.25%	116.005	99.82%	99.92%	99.87%	0.07%
2.597	38.26%	38.57%	38.41%	0.22%	130.159	99.95%	99.99%	99.97%	0.03%
2.914	40.88%	41.12%	41.00%	0.17%	146.041	100.00%	100.00%	100.00%	0.00%
3.269	43.45%	43.62%	43.53%	0.12%					

From the table, for example, only 0.07% of the volume of the powder is in particles smaller than 0.103 $\mu\text{m}$ , 1.04% smaller than 0.206 $\mu\text{m}$ , 7.91% smaller than 0.518 $\mu\text{m}$ , 18.12% smaller than 1.034 $\mu\text{m}$ , and 33.07% smaller than 2.063 $\mu\text{m}$ . The reproducibility of the two tests were excellent, as indicated by the small standard deviation.

Table 4. Cumulative Volume Fractions of  $\text{LiFePO}_4$  Material Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size				Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size			
	Test 1	Test 2	Average	Standard deviation		Test 1	Test 2	Average	Standard deviation
0.073	0.00%	0.00%	0.00%	0.00%	2.914	54.18%	54.23%	54.21%	0.04%
0.082	0.03%	0.03%	0.03%	0.00%	3.269	56.48%	56.51%	56.50%	0.02%
0.092	0.09%	0.10%	0.09%	0.01%	3.668	58.67%	58.69%	58.68%	0.02%
0.103	0.19%	0.22%	0.20%	0.02%	4.116	60.74%	60.77%	60.76%	0.02%
0.116	0.35%	0.39%	0.37%	0.03%	4.618	62.74%	62.77%	62.75%	0.02%
0.130	0.57%	0.62%	0.60%	0.04%	5.182	64.69%	64.72%	64.71%	0.02%
0.146	0.88%	0.95%	0.91%	0.05%	5.814	66.64%	66.67%	66.66%	0.03%
0.164	1.29%	1.37%	1.33%	0.06%	6.523	68.59%	68.64%	68.62%	0.04%
0.184	1.83%	1.93%	1.88%	0.07%	7.319	70.54%	70.62%	70.58%	0.06%
0.206	2.52%	2.64%	2.58%	0.08%	8.213	72.47%	72.57%	72.52%	0.07%
0.231	3.40%	3.53%	3.47%	0.09%	9.215	74.36%	74.46%	74.41%	0.07%
0.260	4.49%	4.62%	4.56%	0.09%	10.339	76.21%	76.28%	76.24%	0.05%
0.291	5.80%	5.94%	5.87%	0.09%	11.600	78.02%	78.05%	78.04%	0.02%
0.327	7.35%	7.48%	7.42%	0.09%	13.016	79.81%	79.81%	79.81%	0.00%
0.367	9.14%	9.25%	9.19%	0.08%	14.604	81.60%	81.58%	81.59%	0.01%
0.412	11.13%	11.23%	11.18%	0.07%	16.386	83.38%	83.37%	83.37%	0.01%
0.462	13.30%	13.39%	13.34%	0.06%	18.386	85.12%	85.14%	85.13%	0.01%
0.518	15.61%	15.69%	15.65%	0.06%	20.629	86.80%	86.84%	86.82%	0.03%
0.581	18.02%	18.10%	18.06%	0.05%	23.146	88.37%	88.42%	88.40%	0.03%
0.652	20.50%	20.58%	20.54%	0.06%	25.970	89.83%	89.85%	89.84%	0.02%
0.732	23.02%	23.11%	23.07%	0.06%	29.139	91.19%	91.19%	91.19%	0.00%
0.821	25.59%	25.69%	25.64%	0.07%	32.695	92.50%	92.48%	92.49%	0.02%
0.921	28.22%	28.33%	28.28%	0.08%	36.684	93.77%	93.73%	93.75%	0.03%
1.034	30.92%	31.03%	30.97%	0.08%	41.160	94.95%	94.93%	94.94%	0.02%
1.160	33.67%	33.78%	33.72%	0.08%	46.182	96.04%	96.04%	96.04%	0.00%
1.302	36.45%	36.55%	36.50%	0.07%	51.817	97.01%	97.05%	97.03%	0.03%
1.460	39.20%	39.29%	39.24%	0.06%	58.140	97.87%	97.95%	97.91%	0.05%
1.639	41.87%	41.95%	41.91%	0.06%	65.234	98.64%	98.73%	98.68%	0.06%
1.839	44.43%	44.51%	44.47%	0.06%	73.194	99.26%	99.34%	99.30%	0.06%
2.063	46.91%	47.00%	46.95%	0.06%	82.125	99.70%	99.75%	99.72%	0.04%
2.315	49.36%	49.44%	49.40%	0.06%	92.146	99.93%	99.94%	99.93%	0.01%
2.597	51.80%	51.87%	51.83%	0.05%	103.389	100.00%	100.00%	100.00%	0.00%
					109.515	100.00%	100.00%	100.00%	0.00%

From the table, for example, only 0.20% of the volume of the powder is in particles smaller than 0.103 $\mu\text{m}$ , 2.58% smaller than 0.206 $\mu\text{m}$ , 15.65% smaller than 0.518 $\mu\text{m}$ , 30.97% smaller than 1.034 $\mu\text{m}$ , and 46.95% smaller than 2.063 $\mu\text{m}$ . The reproducibility of the two tests were excellent, as indicated by the small standard deviation.

**Table 5. Cumulative Number Fractions of Li-Co-PO<sub>4</sub> Mixed-Phase Material  
Smaller than a Particular Particle Size from Two Separate Measurement Runs.**

Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size	Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size
0.075	1.33%	0.671	97.27%
0.080	3.60%	0.711	97.63%
0.085	6.52%	0.753	97.95%
0.090	9.88%	0.798	98.22%
0.095	13.54%	0.845	98.46%
0.100	17.39%	0.895	98.67%
0.106	21.36%	0.948	98.85%
0.113	25.39%	1.005	99.01%
0.119	29.44%	1.064	99.15%
0.126	33.49%	1.127	99.27%
0.134	37.51%	1.194	99.38%
0.142	41.48%	1.265	99.47%
0.150	45.37%	1.340	99.55%
0.159	49.18%	1.419	99.62%
0.169	52.89%	1.503	99.68%
0.179	56.49%	1.592	99.73%
0.189	59.96%	1.686	99.77%
0.200	63.29%	1.786	99.81%
0.212	66.47%	1.892	99.84%
0.225	69.50%	2.004	99.87%
0.238	72.36%	2.123	99.89%
0.252	75.05%	2.249	99.91%
0.267	77.57%	2.382	99.92%
0.283	79.91%	2.523	99.94%
0.300	82.08%	2.673	99.95%
0.318	84.07%	2.831	99.96%
0.336	85.89%	2.999	99.96%
0.356	87.55%	3.177	99.97%
0.378	89.05%	3.365	99.97%
0.400	90.39%	3.564	99.98%
0.424	91.59%	3.776	99.98%
0.449	92.66%	3.999	99.99%
0.475	93.61%	4.236	99.99%
0.503	94.44%	4.487	99.99%
0.533	95.17%	4.753	99.99%
0.565	95.81%	5.035	99.99%
0.598	96.36%	5.333	99.99%
0.634	96.85%	5.649	99.99%
		5.984	100.00%

From the table, for example, only 17.39% of the number of particles are smaller than 0.100 $\mu\text{m}$ , and 63.29% smaller than 0.200 $\mu\text{m}$ .

Table 6. Cumulative Number Fractions of  $\text{LiFePO}_4$  Material Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size	Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size
0.075	1.57%	0.598	97.77%
0.080	4.24%	0.634	98.11%
0.085	7.65%	0.671	98.40%
0.090	11.57%	0.711	98.65%
0.095	15.79%	0.753	98.86%
0.100	20.20%	0.798	99.03%
0.106	24.70%	0.845	99.18%
0.113	29.22%	0.895	99.31%
0.119	33.70%	0.948	99.42%
0.126	38.12%	1.005	99.52%
0.134	42.45%	1.064	99.59%
0.142	46.66%	1.127	99.66%
0.150	50.74%	1.194	99.72%
0.159	54.67%	1.265	99.77%
0.169	58.44%	1.340	99.81%
0.179	62.05%	1.419	99.84%
0.189	65.47%	1.503	99.87%
0.200	68.72%	1.592	99.89%
0.212	71.78%	1.686	99.91%
0.225	74.65%	1.786	99.92%
0.238	77.32%	1.892	99.94%
0.252	79.80%	2.004	99.95%
0.267	82.10%	2.123	99.96%
0.283	84.20%	2.249	99.96%
0.300	86.11%	2.382	99.97%
0.318	87.85%	2.523	99.97%
0.336	89.42%	2.673	99.98%
0.356	90.82%	2.831	99.98%
0.378	92.06%	2.999	99.99%
0.400	93.17%	3.177	99.99%
0.424	94.14%	3.365	99.99%
0.449	94.98%	3.564	99.99%
0.475	95.72%	3.776	99.99%
0.503	96.36%	3.999	99.99%
0.533	96.90%	4.236	100.00%
0.565	97.37%		

From the table, for example, only 20.20% of the number of particles are smaller than 0.100 $\mu\text{m}$ , and 68.72% smaller than 0.200 $\mu\text{m}$ .

## CONCLUSIONS

In this experiment, Li-Co-PO<sub>4</sub> mixed-phase material were synthesized using methods taught in United States Patent #5,538,714 (the "Kamauchi Patent"), and LiFePO<sub>4</sub> material was synthesized using the approaches of the Goodenough research group. Both materials were ground using the method in the Kamauchi Patent. After grinding, both powders were analyzed for particle size distribution. The results clearly indicated that the particles have a broad particle size distribution.

## APPENDIX

### A: US patent 5,538,814 - Lithium Secondary Batteries, Kamauchi et al.

For reference, the relevant parts of US Patent # 5,538,814 (the Kamauchi patent) are highlighted below

#### Example 1

Predetermined amounts of lithium carbonate, basic cobalt carbonate, and 85% phosphoric acid aqueous solution were weighed to fulfill an atomic ratio of Li:Co:P=2:1:1, sufficiently mixed in an alumina crucible, and heated at 900° C in an electric oven for twenty-four hours.

The heated product was identified by X-ray powder diffraction analysis with the use of JCPDS cards. The results of the X-ray analysis showed that the product contained lithium phosphate, lithium-cobalt phosphate, and cobalt oxide at a molar ratio of Li:Co:P=1:0.5:0.5

#### Example 10

The positive electrode active material obtained in Example 1 was further pulverized in a ball mill for 24 hours to adjust the average particle size thereof to about 0.5  $\mu\text{m}$ , and the BET specific surface area to 5  $\text{m}^2/\text{g}$ .

Twenty lithium batteries were fabricated in the same manner as in Example 1 by using this positive electrode.

#### Examples 11, 12

In the same manner as in Example 10 except that the average particle size, and the BET specific surface area of the positive electrode active material were changed as shown in Table 3 by varying the pulverizing time in a ball mill, 20 lithium batteries were fabricated in each Example.

The lithium batteries of Example 10-12 were charged in the same manner as above, and discharge capacity was determined, the results of which are shown in Table 7 wherein the figures are average values.



Partial Table 7

	Active material average particle size ( $\mu\text{m}$ )	BET specific surface area ( $\text{m}^2/\text{g}$ )
Example 10	0.5	5
Example 11	5	1
Example 12	0.01	800

**B. Padhi (1997) article on Phospho-olivines**

The original publication on the use of  $\text{LiFePO}_4$  for lithium secondary batteries is "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries", by A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, Journal of The Electrochemical Society, Vol. 144, issue 4, page 1188-1193 (1997). A copy of this article is attached. For completeness, the most relevant parts of the article are highlighted below.

**Experimental**

$\text{LiMPO}_4$  ( $\text{M} = \text{Mn, Fe, Co, or Ni}$ ) compounds were prepared by direct solid-state reaction of stoichiometric amounts of  $\text{M(II)-acetates}$ , ammonium phosphate, and lithium carbonate.  $\text{LiFePO}_4$  and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) were synthesized in inert atmosphere to prevent the formation of  $\text{Fe}^{3+}$  compounds as impurities. The intimately ground stoichiometric mixture of the starting materials was first decomposed at 300 to 350°C to drive away the gases. The mixture was then reground and returned to the furnace at 800°C for 24 h before being cooled slowly to room temperature.

**C. Particle Size Analysis by Laser Light Scattering conducted a Micromeritics**

Laser light scattering technique utilizes Mie and Fraunhofer Theories to determine particle size distribution from a light scattering pattern. Micromeritics has both the Saturn Digisizer 5200 and the Mastersizer 2000 available for this technique. The Mastersizer 2000 is capable of performing particle size distribution using either the dry dispersion module or wet dispersion module. The Saturn Digisizer 5200 is the highest resolution instrument available, capable of distinguishing small differences in samples. The particle size range is 0.02  $\mu\text{m}$  to 2000  $\mu\text{m}$ .

Available standard tests:

520 - 00

Particle size analysis using an aqueous dispersion. A distribution of particle size diameter is reported between 0.1 to 1000 micrometers. The technique requires at least 2 grams of dry sample material.

520 - 01

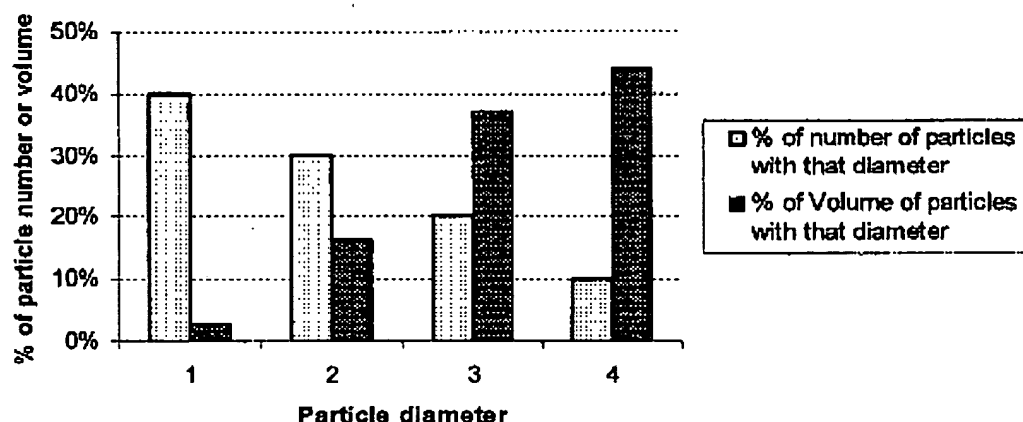
Particle size analysis using a non-aqueous dispersion. A distribution of particle size diameter is reported between 0.1 to 1000 micrometers. The technique requires at least 2 grams of dry sample material.

#### D. Relationship between volume distribution and number distribution

The result of particle size analysis is expressed as a distribution, which states what percentage of the powder sample is in each size range. If the percentage is based on volume of particles, the distribution is a volume distribution. Alternatively, if the percentage is based on number of particles, the distribution is a number distribution. The relationship between the two distributions is illustrated a very simple example.

Assuming there are 4 particles with diameter 1 $\mu$ m, 3 particles with diameter 2 $\mu$ m, 2 particles with diameter 3 $\mu$ m, and 1 particle with diameter 4 $\mu$ m. The volume distribution and the number distribution are calculated in the table below, and shown in the figure below.

Particle Diameter	Number of particles	% of number of particles with that diameter	Vol of each particle	Sum of Vol of particles with that diameter	% of Vol of particles with that diameter
1	4	40%	0.524	2.09	3%
2	3	30%	4.189	12.57	16%
3	2	20%	14.137	28.27	37%
4	1	10%	33.510	33.51	44%
Sum of all particles	10			76.45	



From the example above, it can be understood that number distribution tends to show higher % for smaller particles, and volume distribution tends to show higher % for larger particles. Based on an assumption of uniform particle shape, each distribution can be converted from one representation to the other. As presented above, the particles were assumed to be spherical.

**Craig R. Horne, Ph.D.**

545 Dawn Drive, Sunnyvale, CA 94087 home: (408)733-1783  
 cell: (415)377-6841 e-mail: chorne@alum.berkeley.edu

**Work Experience:**

**November 2005 to Present.** NanoGram Corporation, San Jose, CA. Director, Electrochemical Applications

- Identify new opportunities for applying NanoGram's NanoParticle Manufacturing (NPM™) and Laser Reactive Deposition (LRD™) technology in advanced applications based on electrochemical technology. Areas include batteries, fuel cells, sensors, ultracapacitors, drug delivery, and windows.
- Provide technical strategy and value proposition for Corporate Strategy Team's Opportunity Analysis.
- Technical point-of-contact for US, European, and Japanese customers.
- Manage application developments by leading process development efforts, defining process equipment requirements, and identifying areas for patent coverage. Compose and manage department budget.

**August 2003 to November 2005.** Kainos Energy Corporation, San Jose, CA. Founder and Sr. Vice President, Engineering

- Overall accountability for operations, technical assessment, strategic planning, and fund raising to commercialize fuel cell components and stacks based on novel, LRD™-based approach to fuel cell manufacturing. Lead inventor on LRD™ route to fuel cell manufacturing and enabled novel designs.
- Lead design of equipment and facilities to perform proof of concept for LRD™-process based Solid Oxide Fuel Cell (SOFC) fabrication.
- Wrote successful funding proposal to National Science Foundation for development of SOFC fabrication
- Established connections with several companies (public and private), national labs, and materials characterization labs to support SOFC development.

**February 2003 to August 2003.** Consultant to NanoGram Corporation, San Jose, CA.

- Explored new applications of NanoGram's LRD™ and NPM™ technology. Created value proposition for fuel cell and derivative applications. Efforts led to formation of NanoGram subsidiary, Kainos Energy Corporation, in Aug. 2003.

**August 1998 to February 2003.** NeoPhotonics Corporation and NanoGram Corporation, San Jose, CA.

- Participated in efforts to secure more than \$60 M in venture capital funding comprising lab tours, technology due diligence, and technical presentations to private and corporate investors.
- Director, Materials & Process Engineering (Aug 2002 – Feb 2003). Managed 19 person organization developing novel processes for advanced planar lightwave circuits. Composed operating budget and CapEx plans.
- Manager, Advanced Materials & Methods Group (Dec 2001 – Aug 2002). Built new department to develop novel processes for optical component manufacturing. Designed and budgeted \$0.5M Advanced Materials Development Laboratory. Continued as technical lead for planar amplifier development.
- Senior Scientist, Optical Components (July 2000 – Dec 2001). Lead inventor for NanoGram/NeoPhotonics' planar amplifier technology. Provided technical input and assisted in defining NanoGram/NeoPhotonics' value proposition and business strategy for active optical components.
- Senior Scientist, Nanoscale Energy Storage & Conversion Components (Aug 1998 – June 2000). Defined technical value proposition for use of nanoscale active materials in lithium ion batteries. Developed company-wide capabilities for nanoscale material processing and analysis. Led several projects' developing nanoscale active materials for lithium ion battery applications. Interfaced with US, European, and Japanese customers. Authored several development proposals.
- Technical founder, NanoGram Devices Corporation (NDC). Lead inventor of process for manufacturing nanoscale active material for implantable lithium batteries that formed basis of NDC value proposition.
- Organized & coordinated NanoGram's and NeoPhotonics' summer intern programs using university connections. Program yielded four permanent hires to engineering staff.

**August 1993 to August 1998.** Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA. Graduate Student Research Assistant, Environmental Energy Technologies Division.

- First to correlate degree of covalency with Mn substitution in lithium manganese spinels to explain observed property and performance differences.
- Conceptualized, designed, & implemented new project on X-ray and NMR Spectroscopic analysis of lithium rechargeable battery materials in collaboration with two other academic groups.
- Project included synthesis & characterization of metal-substituted lithium manganese oxides, electrode design, battery cell fabrication & testing.
- Authored over 10 successful proposals for experimental time at US Department of Energy synchrotrons.

Craig R. Horne - CV

- Coordinated & performed X-ray experimentation at synchrotron facilities housed at three DOE National Laboratories: Stanford Synchrotron Radiation Laboratory (Stanford Linear Accelerator Center, Palo Alto, CA), National Synchrotron Light Source (Brookhaven National Lab, Upton, NY), & Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA).

May 1988 to July 1993. AlliedSignal Aerospace Systems & Equipment (now GE Power Systems), Torrance, CA. Engineer, Fuel Cell Engineering Group.

- Primary assignment as member of Solid Oxide Fuel Cell development team. Additional assignments included high- $T_c$  superconductor & whisker-reinforced ceramic composites product development team.
- Co-inventor with N.Q. Minh of thin-film tape calendaring process and stack construction method currently used in GE's SOFC program.
- Responsible for powder preparation, batching, fabrication operations, & single-cell testing for customer-supported Solid Oxide Fuel Cell (SOFC) programs.
- Designed & implemented first process database and quality-control systems for tape-calendar based SOFC component fabrication. Participated in Total Quality Management teams that lowered SOFC component development cycle time by 33%.
- Participated in customer & technical presentations as well as proposal & report writing teams.
- Obtained M.S. at UCLA part-time while working full-time.

#### Education:

Ph.D. in Materials Science & Mineral Engineering; University of California, Berkeley. December 2000.

Thesis Advisor: Elton Cairns; Professor, Department of Chemical Engineering

Dissertation Title: Processing – Structure – Property – Performance Investigations of Lithium Manganese-Based Oxides for Li Rechargeable Batteries.

Minors: Chemical Engineering, Energy and Resources (ERG)

M.S. in Materials Science & Engineering; University of California, Los Angeles. December 1993.

B.S. (with High Honors) in Materials Science & Engineering; University of Florida, Gainesville. May 1988.

#### Honors and Awards:

Summer 1997 Department of Energy/Electrochemical Society Summer Fellow

Fall 1997 U.C. Berkeley University Fellow

Co-winner, Graduate Student Poster Contest, 24<sup>th</sup> Annual Stanford Synchrotron Radiation Laboratory Users Meeting

1998 Daniel Cubicciotti Student Award from The San Francisco Section of The Electrochemical Society

Salutatorian, Department of Materials Science & Engineering, University of Florida, Class of Spring 1988

Honor Societies: Alpha Sigma Mu – President, 1987 to 1988; Tau Beta Pi; Keramos; Florida Blue Key

Deans Lists: College of Liberal Arts & Sciences, U. Florida College of Engineering (4 times); National Deans List

#### Professional and Other Activities:

Electrochemical Society, San Francisco Section – Chair 2005 to 2006, 2000 to 2001, Vice Chair 2004 to 2005,

1999 to 2000, Recording Secretary 1998 to 1999

Electrochemical Society – Individual Membership Committee 2005 to 2007

California Hydrogen Highway – Rollout Strategy Topic Team, Production and Delivery Subgroup

Silicon Valley Energy & Transportation Interest Group

Refereed over 15 papers for *Journal of the Electrochemical Society* and *Electrochemical & Solid State Letters*

U. Florida Lacrosse Club (1984 to 1988): President & Captain 1987 to 1988, Treasurer 1986 to 1987.

U. Florida Homecoming, University Services Division: Director 1987 to 1988, Asst. Director 1986 to 1987.

#### Patent List:

U.S. Patents Awarded

- Patent #6,952,504 - X.X. Bi, E.A. Nevis, R.J. Mosso, M.E. Chapin, S. Chiruvolu, S.H. Khan, S. Kumar, H.A. Lopez, Huy, N.T.T., C.R. Horne, M.A. Bryan, and E.H. Euvrard, *Three Dimensional Engineering of Planar Optical Structures*.
- Patent #6,849,334 - C.R. Horne, P.J. DeMascarel, C.C. Honeker, B. Chaloner-Gill, H.A. Lopez, X.X. Bi, R.J. Mosso, W.E. McGovern, J.T. Gardner, S. Kumar, J.A. Gilliam, V. Pham, E.H. Euvrard, S. Chiruvolu, and J. Jur, *Optical Materials and Optical Devices*.
- Patent #6,749,648 - S. Kumar, C.R. Horne, *Lithium Metal Oxides*.
- Patent #6,732,435 - C.R. Horne, J. Jur, R.J. Mosso, E.H. Euvrard, and X.X. Bi, *Optical Fiber Preforms*.
- Patent #6,482,374 - S. Kumar, H.D. Reitz, C.R. Horne, J.T. Gardner, R.J. Mosso, and X.X. Bi, *Methods for Producing Lithium Metal Oxide Particles*.

Page 2 of 5

Craig R. Horne - CV

6. Patent #6,225,007 - C.R. Horne, S. Kumar, J.P. Buckley, and X.X. Bi, *Metal Vanadium Oxide Particles*.
7. Patent #6,136,287 - C.R. Horne, S. Kumar, H.D. Reitz, J. T. Gardner, and X.X. Bi, *Lithium Manganese Oxides and Batteries*.
8. Patent #5,368,667 - J.V. Guineen, C.R. Horne, and N.Q. Minh, *Preparation of Devices That Include a Thin Ceramic Layer*.
9. Patent #5,290,642 - C.R. Horne and N.Q. Minh, *Method of Fabricating a Monolithic Solid Oxide Fuel Cell*.
10. Patent #5,162,167 - C.R. Horne and N.Q. Minh, *Apparatus and Method of Fabricating a Monolithic Solid Oxide Fuel Cell*.

Twelve U.S. and numerous PCT patent applications in fuel cell fabrication and design, nanoscale materials processing, nanoscale battery materials, nanoscale battery components, photovoltaic cell fabrication, combinatorial discovery, and nanoscale optical materials & structures.

### Journal Papers, Oral Presentations, Conference Proceedings, and Poster Presentations:

#### Journal Papers

1. C.R. Horne, U. Bergmann, M.M. Grush, R.C.C. Perera, D.L. Ederer, T.A. Callcott, E.J. Cairns, and S.P. Cramer, "Electronic Structure of Chemically-Prepared  $\text{Li}_x\text{Mn}_2\text{O}_4$  Determined By Mn X-ray Absorption and Emission Spectroscopies", *Journal of Physical Chemistry B*, 104(2000)9587-9596.
2. C.R. Horne, U. Bergmann, J. Kim, K.A. Striebel, A. Manthiram, S.P. Cramer, and E.J. Cairns, "Structural Investigations of  $\text{Li}_{1-x}\text{Na}_x\text{MnO}_{2.85}\text{I}_{0.12}$  Electrodes by Mn X-Ray Absorption Near Edge Spectroscopy", *Journal of The Electrochemical Society*, 147(2000)395-398.
3. M.M. Grush, C.R. Horne, R.C.C. Perera, D.L. Ederer, S.P. Cramer, E.J. Cairns, and T.A. Callcott, "Correlating Electronic Structure with Cycling Performance of Substituted  $\text{LiMn}_2\text{O}_4$  Electrode Materials: A Study Using the Techniques of Soft X-ray Absorption and Emission", *Chemistry of Materials*, 12(2000)659-664.
4. B. Gee, C.R. Horne, E.J. Cairns, and J.A. Reimer, "Supertransferred Hyperfine Fields at  $^7\text{Li}$ : Variable Temperature  $^7\text{Li}$  NMR Studies of  $\text{LiMn}_2\text{O}_4$ -Based Spinel", *Journal of Physical Chemistry B*, 102(1998)10142-10149.
5. U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, and S.P. Cramer, "Chemical Dependence of Interatomic X-ray Transition Energies and Intensities - a Study of Mn  $K\beta$  and  $K\beta_{2,3}$  Spectra", *Chemical Physics Letters*, 302(1999)119-124.
6. K.S. Striebel, A. Rougier, C.R. Horne, R.P. Reade, and E.J. Cairns, "Electrochemical Studies of Substituted Spinel Thin Films", *Journal of The Electrochemical Society*, 146(1999)4339-4347.
7. U. Bergmann, M.M. Grush, C.R. Horne, P. DeMarois, J.E. Penner-Hahn, C.F. Yocum, D.W. Wright, C.E. Dubé, W.H. Armstrong, G. Christou, H.J. Eppley, and S.P. Cramer, "Characterization of the Mn Oxidation States in Photosystem II by  $K\beta$  X-ray Fluorescence Spectroscopy" *Journal of Physical Chemistry B*, 102(1998)8350-8352.
8. S.P. Cramer, H.-X. Wang, C. Bryant, M. Legros, C.R. Horne, D. Patil, C. Ralston, and X. Wang, "Soft-X-ray Absorption Spectroscopy - Applications to Bioinorganic Chemistry", *ACS Series*, 692(1998)154-178.

#### Oral Presentations

1. U.C. Berkeley NanoConference, Panel on Energy & Nano. Berkeley, CA. April 15, 2006. (Invited Panelist)
2. MIT Club of Northern California's Renewable Energy and Clean Technology Program, Panel on New Business Models in Renewable Energy. Palo Alto, CA. Nov. 3, 2005. (Invited Panelist)
3. C.R. Horne, A. Jaiswal, A. Vu, J. Zhang, L. Acosta, R.B. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "A Disruptive Laser-Based Process for Low Cost SOFC Manufacturing" at the 2005 Fuel Cell Seminar. Palm Springs, CA. Nov. 14-18, 2005.
4. C.R. Horne, "Solid Oxide Fuel Cells" at the MIT-Stanford-Berkeley Nanotechnology Forum's Alternate Energy Technologies for Tomorrow Even!. Palo Alto, CA. July 12, 2005. (Invited)
5. S. Mardini\* and C.R. Horne, "Kainos Energy" at the CleanTech Venture Forum VI. San Francisco, CA. Mar. 22-23, 2005.
6. C.R. Horne, P. de Mascarel, R. Blume, J. Jur, C. Cohen-Jonathan, M. Chapin, J. Posner, W.C. Foo, C. Honeker, Q. Zhu, S. Chiruvolu, R. Mosso, and W. McGovern, "High-Rate Deposition Of Rare-Earth Doped Silicate Nanoparticles For Porous & Dense Optical Films" at the 2005 Spring Meeting of The Materials Research Society. San Francisco, CA. Mar. 28-Apr. 1, 2005.
7. C.R. Horne, "Kainos Energy" at the NanoScience Exchange's Event on Energy Technologies to Reduce Dependence on Foreign Oil. Menlo Park, CA. October 11, 2004. (Invited)
8. C.R. Horne, "Nano-Enabled Fuel Cells" at the NanoSIG Clean Energy and Nano Catalyst Conference. Menlo Park, CA. Aug. 20, 2004.
9. C. R. Horne, "Overview of Lithium Rechargeable Battery Technology & Nanomaterial Applications" at Semi-Therm20. San Jose, CA. Mar. 9-11, 2004. (Invited. Luncheon Plenary)

Craig R. Horne - CV

10. C. R. Horne, P. de Mascarel, R. Blume, S. Chiruvolu, M. Chapin, J. Jur., W. McGovern, R. Mosso, "High-Rate Deposition of Compositionally Complex Nanoparticles for Porous and Dense Films: II. Capabilities" at the 55<sup>th</sup> Pacific Coast Regional & Basic Science Division Fall Meeting of the American Ceramic Society. Oakland, CA. Oct. 19-22, 2003.
11. C. R. Horne, S. Kumar, B. Chaloner-Gill, D. Ghantous, J. Gardner, R. Mosso, N. Kambe, "Processing - Structure - Property - Performance Investigations of Nanocrystalline Materials for Lithium Rechargeable Batteries" at the 55<sup>th</sup> Pacific Coast Regional & Basic Science Division Fall Meeting of the American Ceramic Society. Oakland, CA. Oct. 19-22, 2003. (Invited)
12. C.R. Horne, "Careers in Glass - Integrated Photonic Circuits" at the 2002 Glass & Optical Materials Division Meeting of the American Ceramic Society. Pittsburgh, PA. Oct. 13-16, 2002. (Invited)
13. C.R. Horne, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries" at the 198<sup>th</sup> Meeting of The Electrochemical Society. Phoenix, AZ. Oct. 22-27, 2000.
14. C.R. Horne, U. Bergmann, M.M. Grush, J. Kim, A. Manthiram, S.P. Cramer, K.A. Striebel, and E.J. Cairns, "Structural Studies of Lithium Insertion in Lithium Manganese Oxides" at the 196<sup>th</sup> Meeting of The Electrochemical Society. Honolulu, HI. Oct. 17-22, 1999.
15. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, S.P. Cramer, J.A. Reimer, and E.J. Cairns, "Composition-Structure-Property-Performance Relationship in Mn-substituted  $\text{LiMn}_2\text{O}_4$ " at the 196<sup>th</sup> Meeting of The Electrochemical Society. Honolulu, HI. Oct. 17-22, 1999.
16. C.R. Horne, K.A. Striebel, E.J. Cairns, M.M. Grush, U. Bergmann, and S.P. Cramer, "Atomic & Electronic Structural Consequences of Mn-Substitution in  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  by X-ray Absorption and FTIR Spectroscopies" at the 1997 Fall Meeting of the Materials Research Society. Boston, MA. Dec. 1-5, 1997.
17. C.R. Horne, E.J. Cairns, U. Bergmann, S.P. Cramer, M.M. Grush, and B.J.R. Weiss, "X-ray Spectroscopic Investigations of the Atomic & Electronic Structure of  $\text{Li}_x\text{Mn}_2\text{O}_4$  for Li Rechargeable Batteries" at the 1997 Fall Meeting of the Materials Research Society. Boston, MA. Dec. 1-5, 1997.
18. C.R. Horne, N.Q. Minh, A. Amiro, T.R. Armstrong, J.R. Esopa, J.V. Guisheen, and J.J. Van Ackeren, "Monolithic Solid Oxide Fuel Cell Development: Recent Technical Progress," at the 1992 Fuel Cell Seminar. Tucson, AZ. Nov. 29-Dec. 2, 1992.

## Conference Proceedings Papers

1. C.R. Horne, E. Ooi, R.B. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "Innovative, Laser-Based Process for Development and Manufacturing of SOFCs", in Solid Oxide Fuel Cells IX, S.C. Singhal and J. Mizusaki, eds. Quebec City, Canada, Spring 2005. The Electrochemical Society. PV 2005-07. pp. 466-75
2. C.R. Horne, P. de Mascarel, R. Blume, J. Jur, C. Cohen-Jonathan, M. Chapin, J. Posner, W.C. Foo, C. Honeker, Q. Zhu, S. Chiruvolu, R. Mosso, and W. McGovern, "High-Rate Deposition Of Rare-Earth Doped Silicate Nanoparticles For Porous & Dense Optical Films", in Rare-Earth Doping for Optoelectronic Applications, T. Gregorkiewicz, Y. Fujiwara, M. Lipson, and J.M. Zavada, eds. San Francisco, Spring 2005. Mater. Res. Soc. Symp. Proc. 866, Paper V2.7 (2005).
3. X.X. Bi, S. Kumar, C. Horne, B. Chaloner-Gill, and R. Mosso, "Synthesis of Nanoscale Optical Materials Using Nano Particle Manufacturing (NPM<sup>TM</sup>) Technology", in Optoelectronics, Materials, and Devices for Communications, T.P. Lee and Q. Wang, eds. Proc. SPIE 4580, pp. 103-111 (2001).
4. C.R. Horne, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries" in Rechargeable Lithium Batteries, K.M. Abraham, E.S. Takeuchi, and M. Doyle, eds. Phoenix, Arizona, Fall 2000. The Electrochemical Society. PV 2000-21. pp. 1-7.
5. C.R. Horne, U. Bergmann, M.M. Grush, J. Kim, A. Manthiram, S.P. Cramer, K.A. Striebel, and E.J. Cairns, "Structural Studies of Lithium Insertion in Lithium Manganese Oxides", in Intercalation Compounds for Battery Materials, G. A. Nazri, T. Ohzuku, and M. Thackeray, eds. Honolulu, Hawaii, Fall 1999. The Electrochemical Society. PV 99-24, pp. 41-47.
6. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, S.P. Cramer, J.A. Reimer, and E.J. Cairns, "Composition-Structure-Property-Performance Relationship in Mn-substituted  $\text{LiMn}_2\text{O}_4$ ", in Intercalation Compounds for Battery Materials, G. A. Nazri, T. Ohzuku, and M. Thackeray, eds. Honolulu, Hawaii, Fall 1999. The Electrochemical Society. PV 99-24, pp. 112-120.
7. K.A. Striebel, A. Rougier, C.R. Horne, R.P. Reade and E.J. Cairns, "Characterization Of Pulsed Laser Deposited  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  (Me = Co, Ni) Thin Films For Rechargeable Lithium Batteries" in Lithium Batteries, S. Surampudi and R. A. Marsh, eds. Boston, MA, Fall 1998. The Electrochemical Society. PV 98-16, pp. 263-270.
8. E.J. Cairns, C.R. Horne, B.J. Weiss, M.M. Grush, and S.P. Cramer, "X-Ray Absorption Spectroscopic Investigations of  $\text{Li}_x\text{Mn}_2\text{O}_4$ ", in Proceedings of the 2nd International Symposium on New Materials for Fuel Cells and Modern Battery Systems, Montreal, Canada, July 6-10, 1997. Savadogo, O. and Roherge, P.R., eds., Ecole Polytechnique de Montréal. 1997. pp. 336-347.
9. N.Q. Minh and C.R. Horne, "A Novel Method for Fabricating Thin-Film Ionic & Mixed Conductors" in Proceedings of the 14th RISO International Symposium on Materials Science: High Temperature

Page 4 of 5

Craig R. Horne - CV

- Electrochemical Behavior of Fast Ion & Mixed Conductors, F.W. Poulsen, J.J. Bentzen, T. Jacobsen, E. Shou, and M.J.L. Ostergard, eds. 1993, p. 520.
10. N.Q.Minh, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, and J.J. Van Ackeren, "Tape-Calendered Monolithic & Flat Plate Solid Oxide Fuel Cells," in Proceedings of the Third International Symposium on Solid Oxide Fuel Cells, S.C. Singhal, ed., The Electrochemical Society, Pennington, NJ, 1993, p. 801.
  11. N.Q.Minh, A. Amiro, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, and J.J. Van Ackeren, "Monolithic Solid Oxide Fuel Cell Development: Recent Technical Progress," in 1992 Fuel Cell Seminar Proceedings, Tucson, AZ, 1992, p. 524.
  12. N.Q.Minh, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, F. Liu, T.L. Stillwagon, and J.J. Van Ackeren, "Fabrication Methodologies for Monolithic Solid Oxide Fuel Cells," in Proceedings of the Second International Symposium on Solid Oxide Fuel Cells, F. Gross, P. Zegers, S.C. Singhal, and O. Yamamoto, eds., Commission of the European Communities, Brussels, 1991, p. 93.
  13. N.Q.Minh, J.V. Guiheen, C.R Horne, F. Liu, D.M. Moffatt, T.L. Stillwagon, and J.J. Van Ackeren, "Monolithic Solid Oxide Fuel Cell Technological Status," in 1990 Fuel Cell Seminar Proceedings, Phoenix, AZ, 1990, p. 524.
  14. N.Q.Minh, C.R Horne, F. Liu, D.M. Moffatt, P. Staszak, T.L. Stillwagon, and J.J. Van Ackeren, "Fabrication and Characterization of Monolithic Solid Oxide Fuel Cells," in Proceedings of the 25th IECEC, Reno, NV, 1990, p. 230.
  15. N.Q.Minh, C.R Horne, F. Liu, P. Staszak, T.L. Stillwagon, and J.J. Van Ackeren, "Forming and Processing of Monolithic Solid Oxide Fuel Cells," in Proceedings of the First International Symposium on Solid Oxide Fuel Cells, S.C. Singhal, ed., The Electrochemical Society, Pennington, NJ, 1989, p. 307.

#### Poster Presentations

1. C. R. Horne, A. Jaiswal, A. Vu, J.W. Zhang, L. Acosta, R.E. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "Innovative, Laser-Based Process For Development And Manufacturing Of Solid Oxide Fuel Cells" at SOFC-IX, Quebec City, Canada, May 16-20, 2005.
2. C.R. Horne, E. Ooi, R.E. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "A Disruptive Laser-Based Process for Low Cost Development and Manufacturing of High Performance SOFCs", at 2004 Fuel Cell Seminar, San Antonio, TX, Nov. 1-5, 2004.
3. C.R. Horne, S. Kumar, B. Chaloner-Gill, D. Ghantous, Y. Fortunak, J. Gardner, S. Chiruvolu, K. Hoang, A. Pinoli, J. Xie, H. Reitz, J. Buckley, R. Mosso, X.X. Bi, and N. Kambe, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries via NPM™ Processing" at the NanoSIG™ nanoMaterials & Manufacturing Forum™, Menlo Park, CA, Apr. 24, 2003.
4. C.R. Horne, P. de Mascarel, R. Blume, C. Cohen-Jonathan, J. Jur, W.C. Foo, C. Honeker, M. Chapin, J. Posner, S. Chiruvolu, B. McGovern, Q. Zhu, R. Mosso, and N. Kambe, "Laser Reactive Deposition (LRD™) Processing of Active Glass Films for Planar Waveguide Amplifiers from NanoParticulate-based Coatings" at the NanoSIG™ nanoMaterials & Manufacturing Forum™, Menlo Park, CA, Apr. 24, 2003.
5. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, E.J. Cairns, and S.P. Cramer, "Soft X-ray Spectroscopic Studies of Mn-substituted  $\text{LiMn}_2\text{O}_4$ ", 1998 Advanced Light Source (ALS) Users Meeting, Berkeley, CA, Apr. 1998.
6. C.R. Horne, U. Bergmann, M.M. Grush, K.A. Striebel, E.J. Cairns, and S.P. Cramer, "X-ray Spectroscopic Studies of Lithium Insertion in Lithium Manganese Oxides" at the 24<sup>th</sup> Annual Stanford Synchrotron Radiation Laboratory (SSRL) Users Meeting, Oct. 1997.

**ON K. CHANG, Ph.D.****SUMMARY OF QUALIFICATIONS**

Senior Scientist with 18 years of experience in battery related development, process and product engineering. Hands on expertise in chemical, mechanical and electronic technical areas. Strong background in analytical chemistry, battery technology and application of statistical methods.

**PROFESSIONAL EXPERIENCE**

*NanoGram Corp. San Jose, CA (Technology: nano-particles by laser pyrolysis)*

**Consultant**

1/2006 – present

- Conducted grinding experiments to support a patent application
- Conducted high temperature, solid-state material synthesis.
- Conducted material characterization.
- Developed software for data processing

*Greathatch, Inc., Fremont, CA (Technology: batter, capacitor materials by laser pyrolysis, thermal reactions)*

**Senior Scientist**

1/2004 – 12/2005

- Worked on Silver Vanadium Oxide, Barium Titanium Oxide, and Tantalum powder development programs
- Led overall developments in post-process using laser-pyrolyzed nanopowders in SVO, BTO and Ta projects.
- Improved SVO reactors resulting in 10x better temperature control.
- Designed, fabricated improved tooling for SVO process resulting in better ergonomics and efficiency.
- Maintained SVO production database and developed software for data acquisition, resulting in 75% labor saving.
- Developed software for processing of SVO cell test data, resulting in 90% labor saving.
- Led development of nano-BTO thermal process (grinding, heating), acquired equipment. Fulfilled first deliverable in 3 months, below budget.
- Led development of Ta thermal process (reduction of oxide, sintering), acquired equipment. Fulfilled first deliverable in 6 months.

*Semitec Corporation, Santa Clara, CA (Technology: Dicing blades for singulation of semiconductor dies on wafer)*

**Process Engineer**

2/2002 – 1/2004

- Worked on dicing blades for semiconductor packaging.
- Designed and built low-cost machines for production (centrifuge, burnishing machine). Machines still in used.
- Maintained drawing files for most production tooling and parts. Support other engineers.
- Automated and improved process documentation by using Visual Basic for Excel.
- Resolved production problems in plating, chemical etching, electro-polishing, metrology to ensure efficiency.
- Conducted PM, repair on machine vision systems, interferometers, laser profilers and laser markers.
- Developed new product "beveled wheel", acquired grinding machines and developed process.
- Streamlined and improved process flow for new product "BGA blade". Wrote work instructions and designed travel sheets.

*PolyStor Corporation, Livermore, CA (Technology: Lithium ion batteries with lithium nickel cobalt oxide cathode)*

**Scientist & Program Manager**

4/1998 – 12/2001

- Worked on Li ion  $\text{LiNi}_x\text{Co}_y\text{O}_2$  rechargeable cells with rigid and flexible package.
- Developed electrode coating slurry formulation and process (slurry mixing, homogenizing).
- Developed electrolyte formulation (carbonate ester solvents,  $\text{SO}_2$ , other additives)
- Developed, validated material characterization methods ( $\text{CO}_2$ ,  $\text{OH}$ ,  $\text{NiOOH}$ , other impurities in  $\text{LiNi}_x\text{Co}_y\text{O}_2$ , solvent and additive in coating, water in every component, particle size of powders. Side specific loading of polymer on separator. Pinholes in packing foils, gas in polymer cells).
- Uncovered previously unknown processing problems (bubbles in coating slurry, poor vacuum in drying, water pick-up in storage etc.). Developed monitoring methods.
- Product failure analysis and failure mechanism elucidation (sources of impedance, imbalance).
- Statistical analysis of production & experimental data, trouble shooting. Automated product sorting method.
- Study effects of electrode additives. Elucidate mechanism of additive effects on over-charge protection.
- Managed a \$2M NIST ATP contract for 4 months, coordinated subcontractors, wrote reports to government.



- Participated in quality improvement activities, developed product specs (OCV, impedance, cycle life, fade rate) and incoming material specs (impurities etc), negotiated with vendors.

*Next Century Power, Scotts Valley CA (Technology: Nickel zinc batteries with improved electrolyte)*

#### Research Scientist

1/1995 – 4/1998

- Worked on Ni-Zn rechargeable cells.
- Characterized cell performance (cycle, gassing behavior). Quantified  $H_2$  &  $O_2$  generation separately.
- Dispelled misconception in related technologies (forms of borate in electrolyte)
- Developed electrode ( $ZnO$  &  $Ni(OH)_2$  based) and electrolyte (KOH based) formulation.
- Developed chemical analysis methods (carbonate in  $ZnO$ ).
- Developed processes (carbonate removal in anode, pasting for both electrodes, pre-formation for cathode).
- Studied anti-gassing additives (cationic surfactants).
- Elucidated cell failure mechanisms (area vs. point short due to  $ZnO$  ppt, additive deterioration etc.).
- Worked on various negative electrode grid treatment (cleaning, Pb plating).
- Worked on  $H_2$  recombination in Ni-Zn cell using fuel cell electrode.
- Designed, built low-cost power suppliers, electronic loads, cyclers for cell testing.
- Supervised temporary employees on pilot-line cell builds.

*Valence Technology, San Jose, CA (Technology: Lithium batteries with electron beam polymerized solid electrolyte)*

#### Scientist

10/1990 – 1/1995

- Awarded 16 patents related to battery technology, material characterization.
- Worked on  $Li-V_6O_{13}$  polymer electrolyte rechargeable cells.
- Developed electrode formulation (types and % of carbon, active material).
- Developed material characterization method (polymer precursors in electrolyte by HPLC, IR; Lewis acid in electrolyte by a patent method, dry box atmosphere by UV, conductivity of paste etc).
- Routine and non-routine evaluation of product performance (e.g., shape change, gassing during cycling).
- Developed non-destructive method to quantify gas inside cell package, and automatic method of sorting cells.
- Worked on cathode active material ( $V_6O_{13}$ ,  $LiV_3O_8$ ) synthesis by solid state, sol-gel methods.
- Product failure analysis and failure mechanism elucidation (effect of charge and discharge current, temp, electrolyte conc. on Li dendrite. Surface energy induced Li dendrite growth).
- Mathematical modeling for predicting product performance based on process variables (electron beam polymerizing process, beam dosage, line speed, electrode density, thickness, etc.).

*Altus Corporation, San Jose, CA (Technology: Lithium thionyl chloride, sulfur dioxide, copper chloride batteries)*

#### Scientist

2/1986 – 4/1990

- Awarded 4 patents related to battery technology.
- Worked on  $Li-SOCl_2$  primary,  $Li-SO_2$  primary and  $Li-CuCl_2$  rechargeable cells.
- Studied physical-chemical properties of electrolyte (vapor pressure, conductivity, solubility etc.). Developed tooling for above.
- Developed electrolyte formulation ( $SO_2$ ,  $Cl_2$ ,  $SO_2Cl_2$ , anti-passivation additives in  $SOCl_2$ ).
- Developed electrolyte drying method (converting -OH, purging) resulting in <20ppm water in electrolyte.
- Conducted routine chemical analysis; significantly improved routine AA method.
- Conduct competitor product analysis (cell tear-down, material characterization etc.)
- Supervised pilot plant operation to produce 200 liter electrolyte per day.

#### EDUCATION

Ph.D., Physical Chemistry, 1985, University of California, Davis, CA

B.S., Agricultural Chemistry, 1976, National Taiwan University, Taiwan

#### SPECIALIZED SKILLS

- Battery technology in general, formulation, processing, testing techniques.
- Electrochemistry: various potentiometric, galvanometric, AC impedance techniques.
- Analytical chemistry and powder characterization: Chromatography, Spectroscopy, Wet chemistry, Particle size analysis, Surface area analysis, DSC, TGA
- Physical chemistry: chemical thermodynamics, kinetics.
- Statistics: experimental design & analysis, inference, optimization, mathematical modeling.

- Chemistry in general: organic, inorganic.
- Mechanical design with SolidWorks, shop operation; Electronic design: analog circuits.
- Computer programming skills: Visual Basic for Excel, esp. for data processing, statistics.

#### PATENTS/PUBLICATIONS/PROFESSIONAL ASSOCIATIONS

20 issued patents; 9 publications; numerous corporate & government reports

Member of the Electrochemical Society and the American Chemical Society

#### PERSONAL

US citizen since 1992.

#### PATENTS

- (1) 4,844,993; Additive to improve voltage regulation in Li-CuCl<sub>2</sub> cell
- (2) 4,863,815; Cell design for spirally wound rechargeable Li metal cell
- (3) 4,873,158; Overdischarge protection for rechargeable cells
- (4) 4,892,796; Positive current collector for lithium secondary cells
- (5) 4,902,588; Additive to improve voltage regulation in Li-CuCl<sub>2</sub> cells
- (6) 5,290,702; Method of mapping organic solvent on a surface
- (7) 5,290,704; Method of detecting organic solvent vapor
- (8) 5,304,436; Method for drying a non-aqueous liquid electrolyte
- (9) 5,326,653; Battery unit with reinforced current collector tabs
- (10) 5,354,631; Enhanced lithium surface
- (11) 5,357,786; Device for determining mechanical properties of material
- (12) 5,390,230; Controlled atmosphere sample holder for x-ray diffraction
- (13) 5,426,055; Method to detect decomposition products in Li salt non-aqueous electrolyte
- (14) 5,438,249; State of charge indication by measuring cell thickness
- (15) 5,442,298; Method for measuring resistivity of geometrically undefined material
- (16) 5,453,261; Method of synthesizing high surface area vanadium oxide
- (17) 5,469,069; Method for measuring resistivity of geometrically undefined material
- (18) 5,520,903; Method of making lithium metal oxide cathode active material
- (19) 5,542,163; Electrically conducting adhesion promoter
- (20) 5,545,496; Method of synthesizing filament-like vanadium oxide for rechargeable cell

#### PUBLICATIONS

- (1) C. Cecilio, O. Chang, J. Hall, C. Holliter, J. Morimoto, J. Phillips, and L. Silvester; Performance characteristics of inorganic electrolyte rechargeable cell. Proceedings of the 4th international seminar on lithium batteries. Deerfield Beach, FL; Mar. 1989.
- (2) O. Chang, J. Hall, J. Phillips and L. Silvester; Rechargeable lithium cells with inorganic electrolyte. Proceedings of 33rd international power sources symposium. Electrochemical Society, Cherry Hill, NJ; June 1988.
- (3) O. Chang and P. Rock; Determination of equilibrium constant and  $\Delta S^\circ$  for the reaction  $OD^- + HS^- \rightarrow OH^- + DS^-$ . J. Phys. Chem. 92, 3411 (1988).
- (4) J. Keizer and O. Chang; The non-equilibrium electromotive force, measurement in a continuously stirred tank reactor. J. Chem. Phys. 87, 4064 (1987).
- (5) S. Yee and O. Chang; A simple junction for reference electrodes. J. Chem. Educ. 65, 129 (1988).
- (6) O. Chang; Estimating the equilibrium voltage of an ion-selective electrode. J. Chem. Educ. 64, 91 (1987).
- (7) O. Chang; Why does concentrated Hydrochloric acid fume. J. Chem. Educ. 62, 385 (1985).
- (8) O. Chang; Calculation of the reversibility factor for an irreversible adiabatic process of an ideal gas. J. Chem. Educ. 62, 108 (1985).
- (9) O. Chang; Kinetic models for adiabatic reversible expansion of a monatomic ideal gas. J. Chem. Educ. 60, 647 (1983).

1188

J. Electrochem. Soc., Vol. 144, No. 4, April 1997 © The Electrochemical Society, Inc.

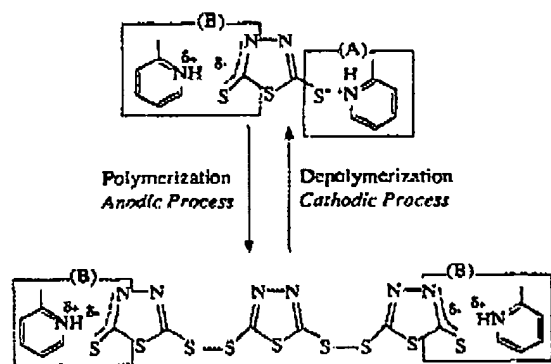


Fig. 5. Proposed structural change of DMCT in PVP film during the oxidation-reduction cycle.

the drawbacks previously mentioned for DMCT electrodes have been overcome by using DMCT/PVP composite films.

#### Acknowledgment

The present work has been financially supported by the Japanese Ministry of Education. K.N. would like to thank Mitsubishi Chemicals for supplying high quality PC solvent.

Manuscript submitted June 19, 1996; revised manuscript received about Dec. 5, 1996.

Tokyo University of Agriculture and Technology assisted in meeting the publication costs of this article.

#### REFERENCES

1. S. J. Visco and L. C. DeJonghe, in *Handbook of Solid State Batteries and Capacitors*, M. Z. A. Munshi, Editor, Chap. 22, World Scientific, NJ (1995).
2. K. Naoi, M. Menda, H. Oolke, and N. Oyama, *J. Electroanal. Chem.*, **318**, 395 (1992).
3. A. Kaminaga, T. Tatsuma, T. Sotomura, and N. Oyama, *This Journal*, **142**, L47 (1995).
4. N. Oyama, T. Tatsuma, T. Sato, and T. Sotomura, *Nature*, **373**, 598 (1995).
5. J. M. Liu, S. J. Visco, and L. C. DeJonghe, *This Journal*, **136**, 2570 (1989).
6. J. M. Liu, S. J. Visco, and L. C. DeJonghe, *ibid.*, **138**, 1891 (1991).
7. J. M. Liu, S. J. Visco, and L. C. DeJonghe, *ibid.*, **138**, 1896 (1991).
8. T. Sotomura, H. Uemachi, K. Takehara, K. Naoi, and N. Oyama, *Electrochim. Acta*, **37**, 1851 (1992).
9. Y. Iwamizu, Y. Oura, and K. Naoi, in *Proceedings of 36th Japanese Battery Meeting*, p. 51 (1995).
10. I. Sekine, K. Kohara, T. Sugiyama, and M. Yusa, *This Journal*, **139**, 3080 (1992).
11. K. Naoi, Y. Oura, Y. Iwamizu, and N. Oyama, *ibid.*, **142**, 354 (1995).
12. S. Picart and E. Genies, *J. Electroanal. Chem.*, **53**, 408 (1996).
13. G. D. Thorn, *Can. J. Chem.*, **38**, 1439 (1960).
14. B. Stanovnik and M. Tisler, *Croat. Chem. Acta*, **37**, 17 (1965).
15. A. J. Bard and L. R. Faulkner, in *Electrochemical Methods, Fundamentals and Applications*, Chap. 3, John Wiley & Sons, Inc., New York (1980).
16. E. M. Genies and S. Picart, *Synth. Met.*, **69**, 165 (1995).
17. M. Mori, Y. Narukawa, W. Kokubo, and K. Naoi, in 1996 Japanese Electrochemical Society Autumn Meeting, p. 16 (1996).

## Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries

A. K. Padhi,\* K. S. Nanjundaswamy,\*\* and J. B. Goodenough

Center for Materials Science and Engineering, The University of Texas at Austin, Austin, Texas 78712-1063, USA

#### ABSTRACT

Reversible extraction of lithium from  $\text{LiFePO}_4$  (triphylite) and insertion of lithium into  $\text{FePO}_4$  at 3.5 V vs. lithium at 0.05 mA/cm<sup>2</sup> shows this material to be an excellent candidate for the cathode of a low-power, rechargeable lithium battery that is inexpensive, nontoxic, and environmentally benign. Electrochemical extraction was limited to ~0.6 Li/formula unit; but even with this restriction the specific capacity is 100 to 110 mAh/g. Complete extraction of lithium was performed chemically; it gave a new phase,  $\text{FePO}_4$ , isostructural with heterosite,  $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ . The  $\text{FePO}_4$  framework of the ordered olivine  $\text{LiFePO}_4$  is retained with minor displacive adjustments. Nevertheless the insertion/extraction reaction proceeds via a two-phase process, and a reversible loss in capacity with increasing current density appears to be associated with a diffusion-limited transfer of lithium across the two-phase interface. Electrochemical extraction of lithium from isostructural  $\text{LiMPO}_4$  (M = Mn, Co, or Ni) with an  $\text{LiClO}_4$  electrolyte was not possible; but successful extraction of lithium from  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  was accomplished with maximum oxidation of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  occurring at  $x = 0.5$ . The  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple was oxidized first at 3.5 V followed by oxidation of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  couple at 4.1 V vs. lithium. The  $\text{Fe}^{2+}$ -O-Mn<sup>2+</sup> interactions appear to destabilize the  $\text{Mn}^{2+}$  level and stabilize the  $\text{Fe}^{3+}$  level so as to make the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  energy accessible.

#### Introduction

Since the demonstration of reversible lithium intercalation between the layers of  $\text{TiS}_2$ ,<sup>1</sup> considerable effort has been devoted to the identification of other lithium-insertion compounds that can be used as the cathode for a secondary lithium battery. The desired material would have a relatively flat open-circuit voltage over a large lithium solid solution within the voltage range of 2.5 <  $V_{oc}$  < 4.0 V and be inexpensive, easy to fabricate, environmentally

benign, and safe in handling and operation. Reversible lithium insertion/extraction has been performed on a variety of compounds containing different transition-metal cations and structural architectures. The sulfides have too low a  $V_{oc}$  and the halides too low an electronic conductivity, so particular attention has been given to transition-metal oxides. These efforts have resulted in the development of rechargeable lithium batteries that now serve as state of the art power sources for consumer electronics.

Among the known Li-insertion compounds, the layered rock salt systems  $\text{Li}_{1-x}\text{CoO}_2$ ,<sup>2</sup>  $\text{Li}_{1-x}\text{NiO}_2$ ,<sup>3</sup> and the manganese-spinel framework system  $\text{Li}_{1-x}(\text{Mn}_2)\text{O}_4$ <sup>4</sup> are now

\* Electrochemical Society Student Member.  
\*\* Electrochemical Society Active Member.

used commercially as 4.0 V positive-electrode materials in rechargeable lithium batteries. However, the voltages in excess of 4.0 V on higher charge in these oxides can lead to the decomposition of the electrolytes, and the fully charged compounds are metastable:  $\text{Mn}_2\text{O}_3$  converts to  $\alpha\text{-MnO}_2$  at 190°C,<sup>8</sup> while fully charged phases of  $\text{Li}_{1-x}\text{CoO}_2$  and  $\text{Li}_{1-x}\text{NiO}_2$  lose  $\text{O}_2$  above 180 and 250°C, respectively.<sup>9</sup> Moreover, a lower lithium mobility within the  $[\text{Mn}_2\text{O}_3]$  spinel framework limits its power capability. Although the  $\text{Li}_{1-x}[\text{Mn}_2\text{O}_3]$  system has a flat  $V_{oc} \approx 3.0$  V vs. lithium, which is attractive,<sup>9</sup> structural changes associated with a cooperative Jahn-Teller deformation of the framework tend to reduce the capacity irreversibly on repeated cycling.<sup>6</sup> In addition, the availability and cost of the transition metals used in these compounds are unfavorable as the  $\text{Wh}/\text{g}$  is a more important figure of merit than  $\text{Wh}/\text{g}$  in the case of large batteries to be used in an electric vehicle or a load-leveling system. These considerations have motivated the investigations of iron-based oxides.

The iron-based oxides containing  $\text{O}^{2-}$  as the anion pose a problem for the cathode designer; in these oxides the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy tends to lie too far below the Fermi energy of a lithium anode and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple too close to it. Layered  $\text{LiFeO}_2$ , prepared by ion-exchange from  $\alpha\text{-NaFeO}_2$ ,<sup>10</sup> has been investigated.<sup>10</sup> It would operate on the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple, but it is metastable and gives unimpressive battery performance. The other iron-based compounds proposed, viz.  $\text{FePS}_4$ ,<sup>11</sup>  $\text{FeOCl}$ ,<sup>12</sup> and  $\text{FeOOH}$ ,<sup>13</sup> have a relatively poor rechargeability and/or too low a discharge voltage. On the other hand, the use of polyanions such as  $(\text{SO}_4)^{2-}$ ,  $(\text{PO}_4)^{3-}$ ,  $(\text{AsO}_4)^{3-}$ , or even  $(\text{MoO}_4)^{2-}$  or  $(\text{WO}_4)^{2-}$  have been shown to lower the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy to useful levels. Among the compounds with NASICON framework, for example, the open-circuit voltages vs. lithium are 3.6 V for  $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$ ,<sup>14</sup> 2.8 V for  $\text{Li}_x\text{Fe}_2(\text{PO}_4)_3$ ,<sup>15</sup> and 3.75 V for  $\text{Li}_x\text{FeTi}(\text{PO}_4)_3$ ,<sup>16</sup> each of these materials has a specific capacity of about 100 mAh/g. Tuning of the energy of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple is accomplished through the choice of the counteranion within the polyanion. Polarization of the electrons of the  $\text{O}^{2-}$  ions into strong covalent bonding within the polyanion reduces the covalent bonding to the iron ion, which lowers its redox energy. The stronger the covalent bonding within the polyanion, the lower is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy and the higher the  $V_{oc}$  vs. lithium for that couple.

The open NASICON framework allows fast  $\text{Li}^+$ -ion diffusion, but a separation of the  $\text{FeO}_6$  octahedra by polyan-

ions reduces the electronic conductivity, which is polaronic in the mixed-valent state. In this paper we report the cathode performance of an iron phosphate having an ordered olivine structure in which the  $\text{FeO}_6$  octahedra share common corners.

The  $\text{M}_2\text{XO}_6$  olivine structure has M atoms in half of the octahedral sites and X atoms in one-eighth of the tetrahedral sites of an hexagonal close-packed (hcp) oxygen array; it is the hexagonal analog of the cubic normal spinel  $\text{X}(\text{M}_2)_4\text{O}_4$ . Olivine crystallizes in preference to spinel for certain small X ions such as  $\text{Be}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ , and occasionally  $\text{Ge}^{4+}$ . Unlike spinel, the two octahedral sites in olivine are crystallographically distinct and differ in size, which favors ordering in  $\text{MM}'\text{XO}_6$  olivines containing M and M' ions of different size and charge. The  $\text{LiMPO}_4$  compounds, with M = Fe, Mn, Co, or Ni, have the ordered olivine structure.

Figure 1 shows the crystal structure of olivine: an ideal hcp model and the actual structure. In the actual structure, the M(1) site has  $\bar{1}$  symmetry, the M(2) octahedron has mirror symmetry with average M-O distances greater than that in the M(1) octahedron. The M(1) sites form linear chains of edge-shared octahedra running parallel to the c-axis in the alternate a-c planes; the M(2) sites form zig-zag planes of corner-shared octahedra running parallel to the c-axis in the other a-c planes (see Fig. 6). Each M(1) site shares its edges with two M(2) sites and two X sites; there is one edge shared by an M(2) site with an X site.<sup>17</sup> Distortion of the hcp oxygen array has been related to the cation-cation coulomb repulsion across the shared edges. In the  $\text{LiMPO}_4$  (M = Mn, Fe, Co, or Ni) compounds, the lithium moieties occupy M(1) sites and the M atoms M(2) sites. With Li in the continuous chain of edge-shared octahedra on alternate a-c planes, a reversible extraction/insertion of lithium from/into these chains would appear to be analogous to the two-dimensional extraction or insertion of lithium in the  $\text{LiMO}_2$  layered oxides with M = Co or Ni. On the other hand, the  $\text{XO}_4$  tetrahedra bridge between adjacent M(2) planes in the olivine structure, which constrains the free volume in which the  $\text{Li}^+$  ions move; only the Li-O bonding constrains the spacing between  $\text{MO}_6$  layers in the  $\text{LiMO}_2$  compounds.

Our attempts to delithiate  $\text{LiMnPO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$  proved unsuccessful with the  $\text{LiClO}_4$  electrolyte used. However, we could use our ability to delithiate  $\text{LiFePO}_4$  to initiate delithiation in the solid-solution system  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ; we report a  $\text{Mn}^{2+}/\text{Mn}^{3+}$  couple at

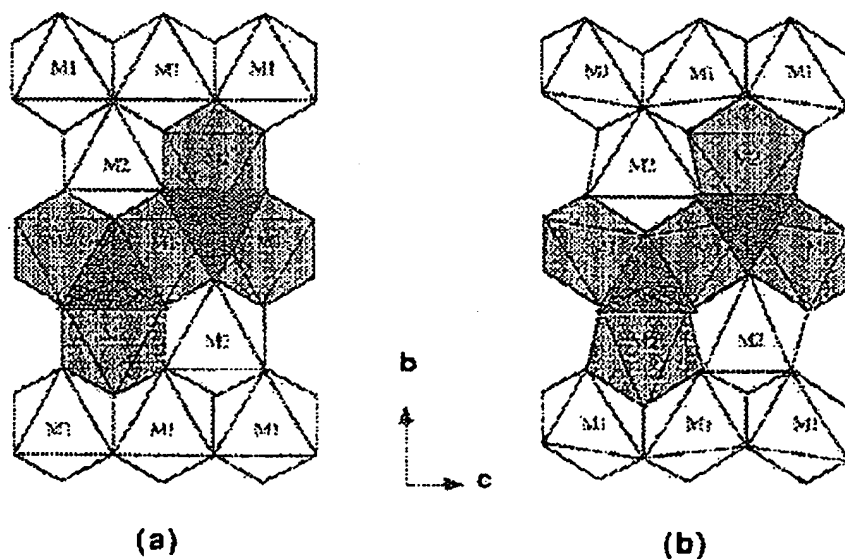


Fig. 1. Olivine crystal structure: (a) ideal HCP model, (b) actual structure.

1190

J. Electrochem. Soc., Vol. 144, No. 4, April 1997 © The Electrochemical Society, Inc.

4.1 eV below the Fermi energy of a lithium anode where there are  $\text{Fe}^{3+}$ -O-Mn $^{2+}$  interactions.

### Experimental

$\text{LiMPO}_4$  ( $M = \text{Mn, Fe, Co, or Ni}$ ) compounds were prepared by direct solid-state reaction of stoichiometric amounts of  $M(\text{II})$ -acetates, ammonium phosphate, and lithium carbonate.  $\text{LiFePO}_4$  and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) were synthesized in inert atmosphere to prevent the formation of  $\text{Fe}^{3+}$  compounds as impurities. The intimately ground stoichiometric mixture of the starting materials was first decomposed at 300 to 350°C to drive away the gases. The mixture was then reground and returned to the furnace at 800°C for 24 h before being cooled slowly to room temperature. The x-ray powder diffraction technique was used to identify the phases. The unit-cell parameters were obtained with a least squares refinement to the diffraction peaks. Rietveld refinement of the x-ray diffraction (XRD) data was performed to obtain the structure.

The electrochemical extraction/insertion of lithium and characterization of the performance of the phospho-olivines as cathodes were made with coin-type cells (Type 2320). After the materials were ground to fine particles with a milling machine, they were mixed/blended with acetylene black and polytetrafluoroethylene (PTFE) in the weight ratio 70:25:5. This cathode mixture, after being kept at 140°C for 2 h, was rolled into thin sheets of uniform thickness and cut into pellets of required size for coin-cell fabrication. The electrolyte was 1 M  $\text{LiClO}_4$  in a 1:1 mixture of propylene carbonate (PC) and dimethoxyethane (DME). A lithium foil was used as the anode. The coin cell was fabricated in a glove box under argon atmosphere.

Chemical delithiation to obtain  $\text{Li}_{1-x}\text{MPO}_4$  ( $0 < x < 1$ ) was performed by reacting the materials with nitronium hexafluorophosphate ( $\text{NO}_2\text{PF}_6$ ) in acetonitrile under inert atmosphere. Reaction of  $\text{LiFePO}_4$  with bromine in acetonitrile was also used to extract lithium chemically. Chemical lithiation was carried out by reacting the material with lithium iodide. The products were washed several times with acetonitrile to ensure the purity of the solid phase before it was dried in vacuum. Atomic absorption spectroscopy was performed on intermediate compositions to obtain the exact lithium content with a Perkin-Elmer 1100 spectrometer.

The thermal stability of the phases was monitored from 50 to 500°C by TGA and DSC techniques on a Perkin-Elmer Thermal Analysis 7 instrument. These experiments were performed in both oxygen and an inert atmosphere.

### Results and Discussion

Electrochemical charge and discharge curves for  $\text{LiFePO}_4$ , Fig. 2, show that approximately 0.8 lithium atoms per formula unit can be extracted at a closed-circuit voltage of 3.5 V vs. lithium and the same amount can be reversibly inserted back into the structure on discharge. The extraction and insertion of lithium ions into the structure of  $\text{LiFePO}_4$  is not only reversible on repeated cycling; the capacity actually increases slightly with cycling.

The placement of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy at 3.5 eV below the Fermi level of lithium in  $\text{Li}_{1-x}\text{FePO}_4$  is to be compared with 2.8 eV found<sup>13,14</sup> in  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Li}_{1-x}\text{FeTi}(\text{PO}_4)_2$  and at 3.6 eV in  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$ .<sup>14</sup> A difference of 0.8 eV between the redox energies in the isostructural NASICON frameworks of  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$  can be attributed to the inductive effect, the oxygen forming a stronger bond within  $(\text{SO}_4)^{2-}$  than in  $(\text{PO}_4)^{3-}$  polyanions. On the other hand, all the oxygen of both  $\text{Li}_{1-x}\text{FePO}_4$  and  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  form strong covalent bonds within a  $(\text{PO}_4)^{3-}$  complex, so the 0.7 eV difference in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energies of these two compounds must have another origin than the inductive effect. For the origin of this difference, we turn to the ionic component of the bonding.

In an ionic compound, the position of the electron energy levels depends critically on the Madelung potential at the different atoms, which depends on both the structure

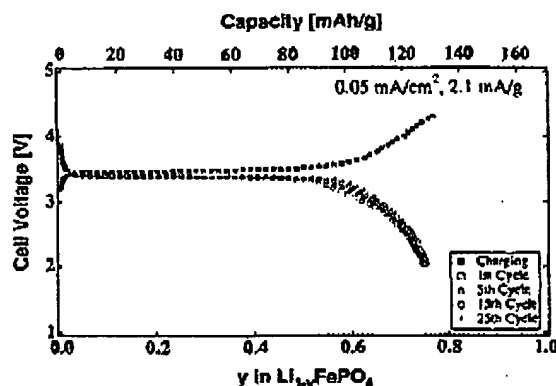
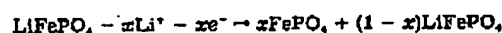


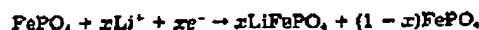
Fig. 2. Discharge/charge curves vs. lithium at 2.0 mA/g ( $0.05 \text{ mA/cm}^2$ ) for  $\text{Li}_{1-x}\text{FePO}_4$ .

and the degree of covalence in the bonding. The Madelung electric field raises the electron energies of the cations and lowers those of anions; in an ionic crystal, the Madelung fields are strong enough to overcome the energy required to create the ionic species, and the redox states are antibonding states of primarily cationic origin. Reference to an  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy implies a substantial ionic component to the bonding; and the stronger the Madelung electric field at the cation site, the higher is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy. The Madelung sum of coulomb energies can account qualitatively for a lower  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy, and hence a higher  $V_{oc}$  vs. lithium in  $\text{Li}_{1-x}\text{FePO}_4$  than in  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$ . In the NASICON framework, the  $\text{FeO}_6$  octahedra share no edges with other cation polyhedra, which reduces the cation-cation coulomb repulsions contributing to the Madelung sum, whereas considerable edge sharing occurs in the ordered olivines. The cation-cation repulsive forces distort the hcp anion array of an olivine, as noted above, but the repulsion is not sufficient to screen the reduction by these forces of the total Madelung electric field that raises the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy above the  $(\text{PO}_4)^{3-}$  energies. Therefore, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  level lies lower in the ordered olivine structure.

The  $V(x)$  curves for  $\text{Li}_{1-x}\text{FePO}_4$  in Fig. 2 show a voltage that is independent of  $x$  over a large range of  $x$ , which indicates, by Gibbs phase rule, that the extraction/insertion reactions proceed by the motion of a two-phase interface. To establish the existence and structure of the second phase, a partial chemical delithiation was performed by reacting  $\text{LiFePO}_4$  with varying amounts  $\text{NO}_2\text{PF}_6$  in acetonitrile. Chemical delithiation allows XRD patterns to be taken on clean samples. The XRD patterns in Fig. 3 show the emergence and growth of a second phase at the expense of  $\text{LiFePO}_4$ , as more and more lithium is extracted. With total chemical delithiation, the second phase could be identified by both chemical analysis and Rietveld refinement to XRD data to be  $\text{FePO}_4$ . XRD patterns for chemical lithiation of  $\text{FePO}_4$ , Fig. 4, show the emergence and growth of  $\text{LiFePO}_4$  at the expense of  $\text{FePO}_4$  on more lithiation. Electrochemical characterization of a cathode made from the  $\text{FePO}_4$  obtained by total chemical delithiation of  $\text{LiFePO}_4$  gave the  $V(x)$  curves of Fig. 5; they are similar to those of Fig. 2, thus confirming that  $\text{FePO}_4$  is the second phase that is present on electrochemical extraction of lithium from  $\text{LiFePO}_4$ . Therefore the extraction of lithium from  $\text{LiFePO}_4$  to charge the cathode may be written as



and the reaction for the insertion of lithium into  $\text{FePO}_4$  on discharge as



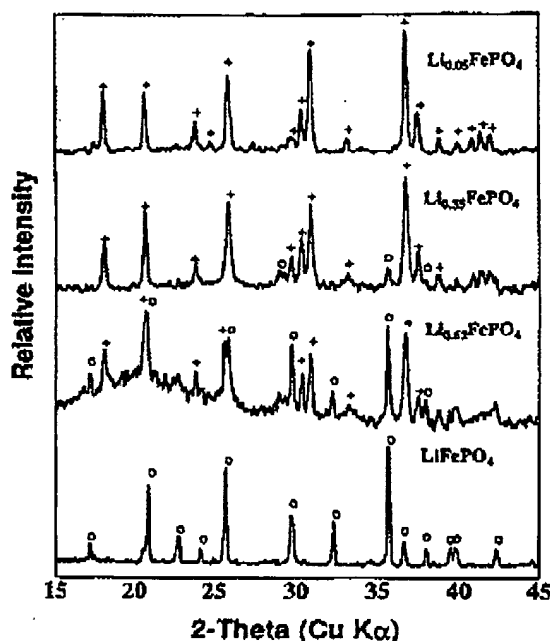


Fig. 3. Chemical delithiation of  $\text{LiFePO}_4$ . XRD patterns showing the emergence and growth of the second phase  $\text{FePO}_4$ .

The excellent reversibility of the cells on repeated cycling is due to the striking similarity of the  $\text{LiFePO}_4$  and  $\text{FePO}_4$  structures, which are compared in Fig. 6.  $\text{FePO}_4$  is isostructural with heterosite,  $\text{Fe}_{0.99}\text{Mn}_{0.01}\text{PO}_4$ , for which several bond lengths have been refined.<sup>19</sup> The lattice

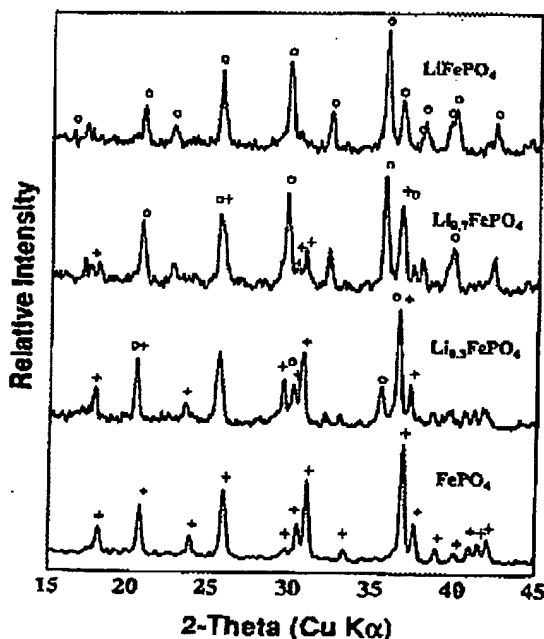


Fig. 4. Chemical lithiation of  $\text{FePO}_4$ . XRD patterns showing the emergence and growth of the second phase  $\text{LiFePO}_4$ .

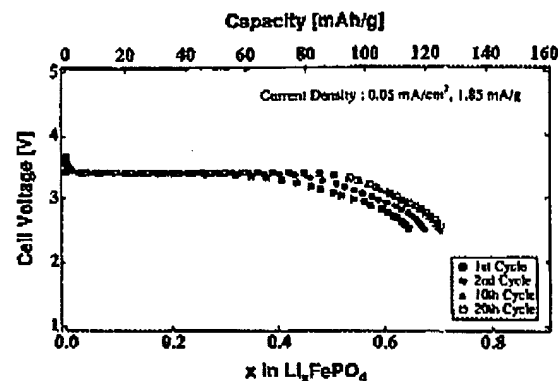
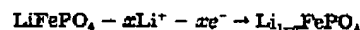


Fig. 5. Discharge/charge curves vs. lithium at 2.0 mA/g ( $0.05 \text{ mA/cm}^2$ ) for  $\text{LiFePO}_4$ .

parameters and the space group of both  $\text{LiFePO}_4$  and  $\text{FePO}_4$  phases are listed in Table I; both  $\text{LiFePO}_4$  and  $\text{FePO}_4$  have the same space group. On chemical extraction of lithium from  $\text{LiFePO}_4$ , there is a contraction of the  $a$  and  $b$  parameters, but a small increase in the  $c$  parameter. The volume decreases by 6.81% and the density increases by 2.59%. Although the changes in the  $\text{FePO}_4$  framework are displacive, not diffusional, a first-order transition between  $\text{LiFePO}_4$  and  $\text{FePO}_4$  prevents the continuous insertion reaction



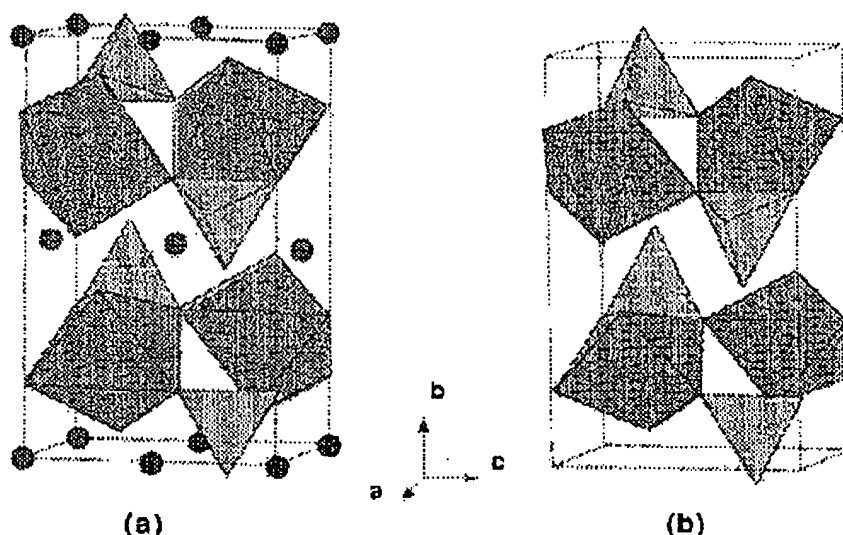
A first-order transition would seem to require a cooperative elastic deformation of the  $\text{FePO}_4$  framework. It is therefore of interest that the principal change in the framework on delithiation is a cooperative adjustment of the framework to the coulombic repulsion between the  $\text{O}^{2-}$  ion sheet interfacing the delithiated planes.

Insertion of lithium into  $\text{FePO}_4$  was reversible over the several cycles investigated.  $\text{Li}_x\text{FePO}_4$  represents a cathode of good capacity, and it contains inexpensive, environmentally benign elements. However, a nearly close-packed hexagonal oxide-ion array that is bonded strongly in three dimensions provides a relatively small free volume for  $\text{Li}^+$  ion motion, so the electrode supports only relatively small current densities at room temperature. Nevertheless, increasing the current density does not lower the open-circuit voltage  $V_{oc}$ ; rather it decreases, reversibly, the cell capacity. Reducing the current restores the capacity. This observation indicates the loss in capacity is a diffusion-limited phenomenon associated with the two-phase character of the insertion process.

As is illustrated schematically in Fig. 7, lithium insertion proceeds from the surface of the particle moving inward behind a two-phase interface, a  $\text{Li}_x\text{FePO}_4/\text{Li}_{1-x}\text{FePO}_4$  interface in this system. As the lithiation proceeds, the surface area of the interface shrinks. For a constant rate of lithium transport per unit area across the interface, a critical surface area is reached where the rate of total lithium transported across the interface is no longer able to sustain the current; the cell performance becomes diffusion-limited. The higher the current, the greater is the total critical interface area and, hence, the smaller the concentration  $x$  of inserted lithium before the cell performance becomes diffusion-limited. On extraction of lithium, the parent phase at the core of the particle grows back toward the particle surface, which is why the parent phase is retained on repeated cycling and the loss in capacity is reversible on lowering the current density delivered by the cell. This loss of capacity is not due to a breaking of the electrical contact between particles as a result of volume changes, a process that is normally irreversible.

1192

J. Electrochem. Soc., Vol. 144, No. 4, April 1997 © The Electrochemical Society, Inc.

Fig. 6. Crystal structures of (a)  $\text{LiFePO}_4$  and (b)  $\text{FePO}_4$ .

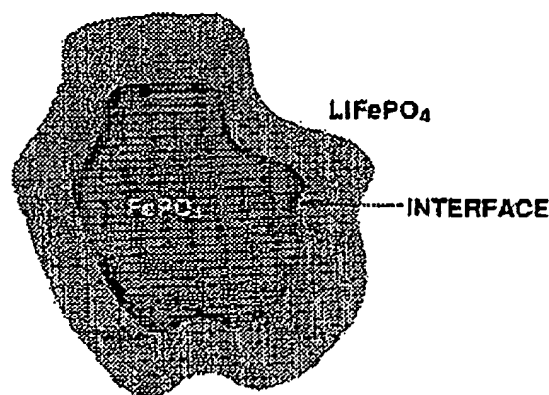
The thermal stability of the fully charged state of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$ , is shown in the TGA curves of Fig. 8. On thermal treatment of  $\text{FePO}_4$  in nitrogen atmosphere up to  $350^\circ\text{C}$ , there was no appreciable change in the weight. A weight loss of 1.6% is observed when the sample was heated up to  $500^\circ\text{C}$ . There was very little difference in the TGA curves when the sample was heated in oxygen atmosphere. No appreciable change could be found in the XRD patterns taken after thermal treatment; there was no trace of impurity. Since the  $\text{FePO}_4$  for these experiments was prepared by treating  $\text{LiFePO}_4$  with bromine several times in acetonitrile, there could be a small amount of  $\text{LiBr}$  in the sample even after washing the products several times with acetonitrile, which decomposes at  $350^\circ\text{C}$ . The DSC curve shows a small reversible peak at  $300^\circ\text{C}$  of unknown origin.

In order to locate the  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ,  $\text{Co}^{2+}/\text{Co}^{3+}$ , and  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox energies with respect to the Fermi energy of lithium, we tried to extract lithium electrochemically from other  $\text{LiMPO}_4$  compounds with  $\text{M} = \text{Mn}, \text{Co}, \text{or Ni}$ . Since  $\text{LiClO}_4$  with 1:1 by volume mixture of PC and DME was used as the electrolyte, the upper voltage limit used in our experiments were 4.3 to 4.4 V. Higher upper voltages resulted in oxidation of the electrolyte, and we could not initiate access to the  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ,  $\text{Co}^{2+}/\text{Co}^{3+}$ , and  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox couples in these compounds. However, we could access the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  couple in the presence of some iron atoms in the structure. Solid-solutions  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  with  $x = 0.25, 0.50$ , and  $0.75$  were synthesized. Figure 9 shows linear increases of the lattice parameters with increasing Mn content in the structure, in accordance with Vegard's law.

Figure 10a-d show the electrochemical charge and discharge curves for coin-type cells with  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50, 0.75$ , and  $1.0$ ) as the cathode and lithium as the anode. The charging curve for  $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ , Fig. 10a, shows a small plateau at 4.1 V, which is not very distin-

guishable in the discharge curve. For  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ , the charging curve Fig. 10b shows two distinct plateaus of almost equal width, and these plateaus are reproducible on discharge and over repeated cycling. As the Mn content is increased in the structure, the amount of lithium that can be electrochemically extracted by charging decreases as is evident in Fig. 10c for  $\text{LiFe}_{0.25}\text{Mn}_{0.75}\text{PO}_4$ . With all the Fe atoms replaced by Mn atoms as in  $\text{LiMnPO}_4$ , lithium could not be extracted either electrochemically, Fig. 10d, or chemically by reacting with  $\text{NO}_2\text{PF}_6$  in acetonitrile.

From these observations, we conclude that the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couple in phospho-olivines lies 4.1 eV below the Fermi energy of lithium if the Mn atoms have an Fe atom as a nearest neighbor. Destabilization in the presence of iron of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couple from over 4.3 to 4.1 eV below the Fermi energy of lithium could reflect the  $\text{Fe}^{3+}$ -O-Mn<sup>2+</sup> superexchange interaction; the  $\text{Mn}^{2+}$  level would be antibonding and the  $\text{Fe}^{3+}$  level bonding with respect to this interaction. In  $\text{LiMPO}_4$ , with  $\text{M} = \text{Co}$  and  $\text{Ni}$ , the  $\text{M}^{2+}/\text{M}^{3+}$  redox energies lie well below the highest occupied molecular orbital of our electrolyte, with the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox couple lying around 0.6 eV below the  $\text{Co}^{2+}/\text{Co}^{3+}$  redox couple as in the case of the inverse spinels  $\text{VLiM}[\text{O}]_2$ .

Fig. 7. Schematic representation of the motion of  $\text{LiFePO}_4/\text{FePO}_4$  interface on lithium insertion to a particle of  $\text{FePO}_4$ .Table I. The space group and lattice parameters of  $\text{LiFePO}_4$  and delithiated phase  $\text{FePO}_4$ .

	$\text{LiFePO}_4$	$\text{FePO}_4$
Space Group	Pb nm	Pb nm
a (Å)	6.098 (3)	5.792 (1)
b (Å)	10.334 (4)	9.821 (1)
c (Å)	4.693 (1)	4.788 (1)
Volume (Å <sup>3</sup> )	291.392 (8)	272.357 (1)

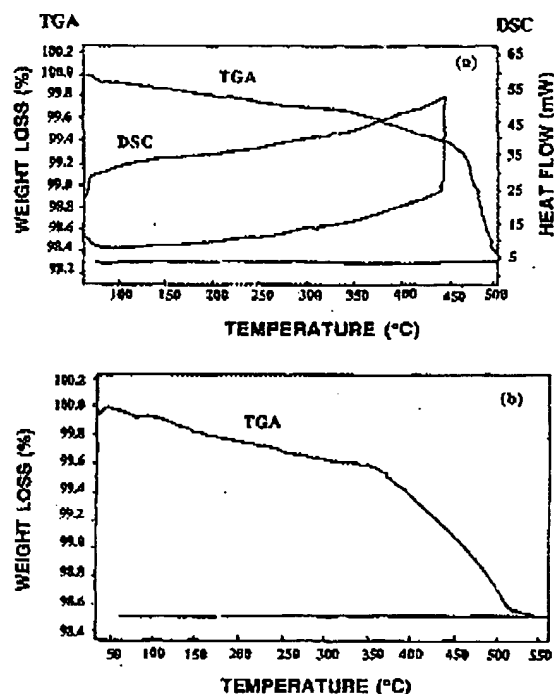


Fig. 8. The thermal stability of dehydrated phase  $\text{FePO}_4$ : (a) TGA and DSC curves in nitrogen atmosphere and (b) TGA curve in oxygen atmosphere.

with  $M = \text{Co}$  or  $\text{Ni}$ .<sup>18</sup> It appears that the greater covalence of the  $\text{PO}_4$  tetrahedron relative to that of the  $\text{VO}_4$  tetrahedron not only favors the olivine as against the spinel structure; it also stabilizes the redox couples at the octahedral sites by at least 0.4 eV, lowering the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  couple from 3.7 eV below the lithium-anode Fermi energy in  $\text{V}(\text{LiMn})\text{O}_4$  to 4.1 eV in  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ .<sup>20</sup>

### Conclusion

On extraction of lithium from  $\text{LiFePO}_4$ , a flat closed-circuit voltage (CCV) curve at 0.05 mA/cm<sup>2</sup> of 3.5 V vs. lithium is obtained for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple due to the presence of two phases,  $\text{LiFePO}_4$  and  $\text{FePO}_4$ . These phases belong to the same space group with a variation of the  $\text{FePO}_4$  host only in the unit-cell parameters. This material is very good for low-power applications; at higher current densities there is a reversible decrease in capacity that, we suggest, is associated with the movement of a two-phase interface, a feature characteristic of cathodes that traverse a two-phase compositional domain in the discharge cycle. The intercalation of only 0.6 Li atom/formula unit of  $\text{LiFePO}_4$  may be an extrinsic problem since the same  $V(x)$  curves are obtained starting with  $\text{FePO}_4$  and essentially all the lithium can be extracted chemically from  $\text{LiFePO}_4$ .

The deintercalation of lithium from the solid solution  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0$  to 1) allows location of the position of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couple. When  $x = 0$ , we get a plateau at 3.5 V; but as the manganese content is increased, a plateau at 4.1 V appears. Maximum charging at 4.1 V is accomplished for  $x = 0.5$ . As expected, we observe that the oxidation of  $\text{Mn}^{2+}$  occurs only after the oxidation of  $\text{Fe}^{2+}$ . We were unable to take out any lithium from  $\text{LiMnPO}_4$ , while charging up to 4.3 V. Moreover, the width of the 4.1 V plateau decreases with increasing  $x > 0.5$ , which suggests that the 4.1 V plateau is associated with the Mn atoms having Fe near neighbors. It appears that the Mn-O-Fe interactions raise the energy of the

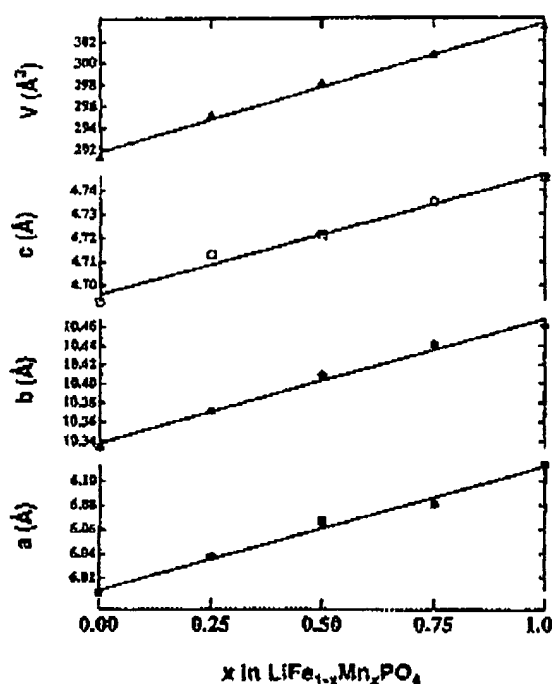


Fig. 9. Variation of lattice parameters of  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  with increasing Mn content in the structure.

$\text{Mn}^{2+}/\text{Mn}^{3+}$  couple and slightly lower the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple. We were unable to extract Li from isostructural  $\text{LiCoPO}_4$  and  $\text{LiNiPO}_4$  with the electrolyte  $\text{LiClO}_4$  in PC and DME due to the stability of the  $\text{Co}^{2+}/\text{Co}^{3+}$  and  $\text{Ni}^{2+}/\text{Ni}^{3+}$  couples.

### Acknowledgment

We thank the Robert A. Welch Foundation, Houston, Texas, for financial support.

Manuscript submitted Sept. 5, 1996; revised manuscript received Dec. 15, 1996.

The University of Texas at Austin assisted in meeting the publication costs of this article.

### REFERENCES

1. M. S. Whittingham, *This Journal*, **123**, 315 (1976).
2. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.*, **15**, 783 (1980).
3. M. G. S. R. Thomas, W. I. F. David, and J. B. Goodenough, *ibid.*, **20**, 1137 (1985).
4. T. Ohzuku, M. Kitagawa, and T. Hirai, *This Journal*, **137**, 769 (1990).
5. J. M. Tarascon and D. Guymard, *Electrochim. Acta*, **38**, 1221 (1993).
6. J. R. Dahn, E. W. Fuller, and U. von Sacken, *Solid State Ionics*, **69**, 265 (1994).
7. M. M. Thackeray, F. J. Johnson, L. A. de Picciotto, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, **19**, 179, (1984).
8. M. M. Thackeray, A. de Kock, M. H. Rossouw, D. Liles, R. Bittih, and D. Hoge, *This Journal*, **139**, 363, (1992).
9. V. B. Nalbandyan and I. L. Shukacv, *Russ. J. Inorg. Chem.*, **32**, 3, (1987).
10. Y. Takeda, K. Nakahara, M. Nishijima, N. Imanashi, O. Yamamoto, M. Takano, and R. Kanno, *Mater. Res. Bull.*, **29**, 659 (1994).
11. A. Le Mehaute, G. Ouvrard, R. Brec, and J. Rouxel, *ibid.*, **12**, 1191 (1977).
12. M. S. Whittingham, *Prog. Solid State Chem.*, **12**, 41 (1978).
13. R. Brec and A. Dugast, *Mater. Res. Bull.*, **15**, 619 (1980).



1194

J. Electrochem. Soc., Vol. 144, No. 4, April 1997 © The Electrochemical Society, Inc.

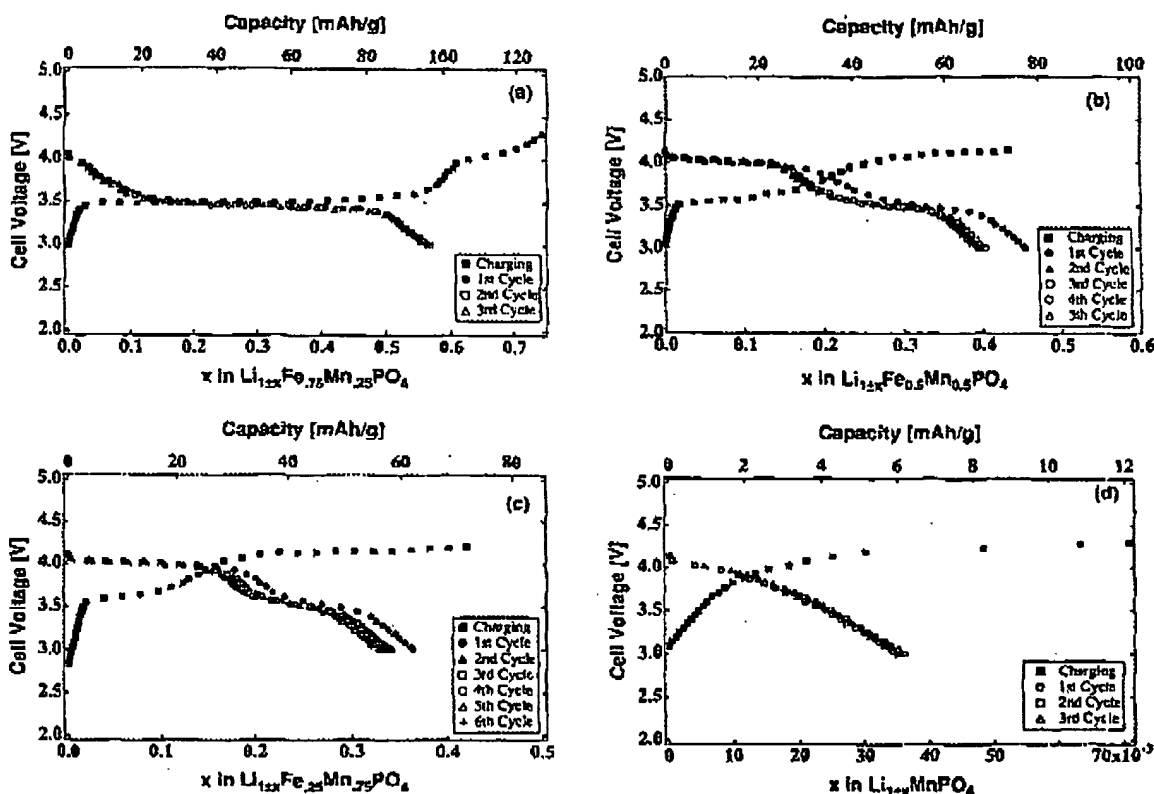


Fig. 10. Discharge/charge curves vs. lithium at current densities 2.0 mA/g, [0.05 mA/cm<sup>2</sup>] for (a)  $\text{LiFe}_{0.7}\text{Mn}_{0.3}\text{PO}_4$ , (b)  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ , (c)  $\text{LiFe}_{0.3}\text{Mn}_{0.7}\text{PO}_4$ , and (d)  $\text{LiMnPO}_4$ .

14. S. Okada, K. S. Nanjundaswamy, A. Manthiram, J. B. Goodenough, H. Ohtsuka, H. Arai, and J. Yamaki, in *Proceedings of 36th International Power Sources Symposium*, p. 110, Cherry Hill, NJ (1994).
15. C. Masquelier, A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Solid State Chem.*, Submitted.
16. A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, and J. B. Goodenough, in *Proceedings of 37th International Power Sources Symposium*, p. 180, Cherry Hill, NJ (1996).
17. G. E. Brown, Ph.D. Thesis, Virginia Polytechnic Institute, Blacksburg, VA (1970).
18. W. Evantoff, R. Martin, and D. R. Peacor, *Am. Min.*, 57, 45 (1972).
19. G. T. Fey, Wu Li, J. R. Dahn, *This Journal*, 141, 2279 (1994).
20. A. K. Padhi, W. B. Archibald, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Solid State Chem.*, In press.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**